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Generation and fate of volatile organic sulfur compounds during anaerobic digestion of waste activated sludge

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ABSTRACT

This study investigates the generation and fate of volatile organic sulfur compounds (VOSCs) during biodegradation of waste activated sludge under anaerobic conditions. Experiments involved the operation of laboratory-scale anaerobic digesters at a solid retention time of 20 d. Concentration profiles of methanethiol, dimethyl sulfide (DMS), dimethyl disulfide, and hydrogen sulfide were monitored. Methanethiol (MT) and DMS are the main organic sulfur compounds exhibiting consecutive increase/decline phases. In the second step, aliquots taken from bioreactors were supplemented with two sulfur-containing amino acids, cysteine, and methionine. The results suggest that the biodegradation of the two sulfur-containing proteins are the primary source of hydrogen sulfide, methanethiol, and DMS generation. Finally, ethyl-2-butynote was added to aliquots taken from the bioreactors to explore the role of methanogenic activity. Methane production is stopped, and resulting MT and DMS profiles are no longer included as a declining phase. The results suggest that sulfur amino acids are a potential primary source for the formation of MT and DMS that were subsequently degraded by methanogens. Therefore, reducing proteins containing sulfur amino acids along with increasing methanogenic activity appears to be an effective strategy to control VOSCs and the associated odor problem.

Keywords: Volatile organic sulfur compounds; Hydrogen sulfide; Metanogenic activity; anaerobic digestion; Waste activated sludge

1. Introduction

Until recently, while substantial research effort was devoted to novel processes for wastewater treatment and disposal, a much lower emphasis was placed on different issues related to sludge disposal [1–4]. It is impossible to avoid the formation of sewage sludge with the existing state of waste management technology [5]. However, the current EU perspective regarding waste as a resource created a new sludge management strategy, mainly involving recycle and reuse options [6]. These options generally included energy-based alternatives as such pyrolysis, gasification, incineration, etc., all alternatives to basic landfilling [7–11]. Despite EU efforts toward developing sustainable alternatives for final disposal of municipal sludge, landfilling will still be the most applied disposal method: currently, more than 50% of municipal sludge produced in Europe goes to landfilling sites [12,13].

One of the major issues that critically restrict land application practice is the generation of odor-causing compounds

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and the nuisance caused by their emissions [14,15]. Volatile organic sulfur compounds (VOSCs) are the key parameters associated with odors production as part of landfilling practice [16]. These compounds mainly include methanethiol (MT), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS). Also, Novak et al. [17] have reported that VOSCs are produced from anaerobically digested sludge; they observed that VOSC emission profiles exhibit an initial increase until a peak value, followed by decline and total depletion. They also argued that the characteristics of odor-causing compounds would determine the odor potential of the sludge stored in landfill sites. Under anaerobic conditions, the VOSC profiles reflected a balance between their production and degradation [18]. Therefore, when steady-state is reached, the rate of VOSCs generation equals the rate of degradation, resulting in a low emission rate. This indicates that VOSC serves as a substrate for methanogens under anaerobic conditions. The metabolic pathways for methane production for both hydrogenotrophic and acetoclastic methanogens have indicated that DMS (CH_3–S–CH_3) available in digesters directly serve as a metabolic intermediate for both hydrogenotrophic and acetoclastic methanogen; the methyl group was transferred to coenzyme *M* to generate methyl-coenzyme *M* and methanethiol (CH_3–SH) [19,20]. Therefore, system disturbance and/or inhibition of metanogenic activity would increase VOSC emission. Matthews and Goulding [21] reported that a system disturbance by introducing toxicants such as 2-nitroethanol (2NEOH); sodium nitrate (SN); or salts, resulted in the release of VOSCs and caused odors problems. Similarly, Iranpour et al. [22] observed significant MT generation during thermophilic digestion. They argued that the temperature of the thermophilic stage could result in an immediate increase in MT concentration. This could imply a slower methanogenic activity for VOSCs degradation. However, when the temperature was reduced, the odor problems and high MT concentrations were considerably relieved. Levén et al. [23] investigated the effect of temperature on both the bacterial and archaeal community structure in two methanogenic bioreactors operating at 37°C and 55°C, respectively, and degrading the same complex substrate; source-separated organic household waste. They did not study the impact of iron or aluminum addition into the biological reactor on the efficiency of anaerobic digestion and the generation of odor emitting compounds. Lyimo et al. [24] investigated the oxidation of dimethylsulfide and methanethiol by sulfate-reducing bacteria (SRB) in Tanzanian mangrove sediments. They did not investigated the effect of pretreatment of waste activated sludge (WAS) prior to anaerobic digestion on the volatile sulfur compounds in biogas. They observed 37%–46% H_2S reduction in biogas by different combinations of hydrogen peroxide; ferrous chloride and mechanical processes. In a similar study, Park and Novak [25] tested thermo-oxidative pretreatment of municipal WAS at 60°C with oxidants, which caused a 75% and 40% reduction in H_2S and DMS concentrations respectively. Higgins et al. [26] interpreted VOSC generation processes through mesophilic and thermophilic digestion of methionine; the results showed the direct generation of only methanethiol (MT), which was methylated to form DMS and subsequently degraded to H_2S. They also indicated that thermophilic conditions could be more problematic for VOSC control. Also, studies using molecular techniques to investigate the changes in the profiles of methanogenic communities suggested that increasing temperature could be associated with changes in the methanogenic population [27]; sulfate-reducing microorganisms could oxidize DMS and methanethiol (MT) to carbon dioxide and hydrogen sulfide with sulfate serving as a terminal electron acceptor [28].

At this point, it should be noted that related research mostly reflects empirical efforts tackling different aspects of the subject. While this work should always be praised for the experience and ingenuity that always accompany successful empiricism, the available information is still too diverse to provide a comprehensive understanding of factors influencing the fate of VOSC under anaerobic conditions. This study offers a novel perspective by providing the necessary basic scientific insight to mechanisms responsible for the generation of VOSC, mainly by assessing the fate of selected sulfur-containing amino acids under anaerobic conditions.

In this context, the objective of this study is to precisely investigate the generation and fate of these compounds during anaerobic digestion of treatment sludge, with specific emphasis on the effect of sulfur-containing amino acids and the role of methanogenic activity and biogas generation.

2. Materials and methods

2.1. Experimental rationale

The adopted experimental program included three consecutive steps to evaluate the generation and fate of VOSCs, under anaerobic conditions. In the first step, the evolution of three major organic sulfur compounds, namely, MT, DMS, and DMDS were observed together with hydrogen sulfide (H_2S) in laboratory-scale anaerobic bioreactors fed with WAS and sustained under steady-state conditions at a solid retention time (SRT) of 20 d. Methanethiol, the DMS, DMDS, and the hydrogen sulfide are the major compounds of sulfur transformations under anaerobic conditions. Obviously, omitting one compound would leave an important phase obscure and may result in misleading evaluations. The operation of bioreactors was monitored for more than 60 d to obtain the concentration profiles of these compounds. In the second step, aliquots taken from bioreactors were supplemented with two sulfur-containing amino acids, L-cysteine (Cys), and L-methionine (Met). Their accelerating impact on the generation of MET and DMS was followed for a period of around 20 d to allow comparison with the previous anaerobic bioreactor operation. In the last phase, ethyl-2-butynote (EB), acting as an inhibitor to methanogens, was added into aliquots taken from the bioreactors to explore the role of methanogenic activity on the fate of MT and DMS.

2.2. Experimental setup

The WAS used in this study was taken from the secondary clarifiers of a municipal wastewater treatment plant (WWTP) located in Bangkok Thailand. The sludge was settled at 4°C for 24 h. Measurement of the sludge pH was between 6.8 and 7.1. The experiments involved the operation of three parallel

anaerobic bioreactors. The nominal volume for each reactor was 10 with 5 L active volume. The bioreactors were initially seeded with the settled sludge with 4% total suspended solids (TSS). The reactors were operated at 20 d SRT and the temperature was kept at 35°C. Gases circulated from headspace to the bottom of the reactor provided mixing for each reactor. The reactors were fed daily using sludge taken from the WWTPs: the sludge fed to bioreactors consisted of 1:1 ratio of primary and secondary sludge on total solids (TS) basis. The reactors were operated at steady-state as indicated by low variation (5%) of gas production.

2.3. Experiments with amino acid addition

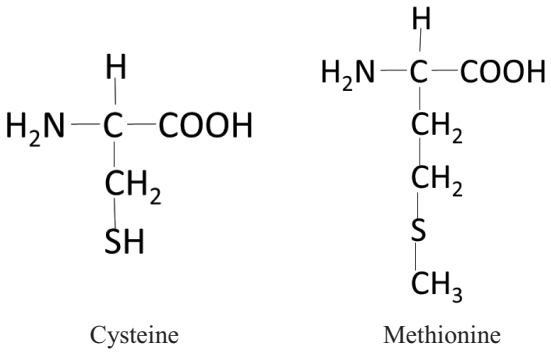
This part of the experiments was conducted to see the influence of sulfur-containing amino acids on the production of odor-causing compounds. At steady-state, two 150 mL samples were taken from bioreactor 1 and placed in two different serum bottles (300 mL), one serving as a control for the other. A dose 0.05 mmols L-cysteine (Cys), an amino acid containing sulfur in the side chain, was introduced to the bottle that did not serve as a control. Then, the generation of MT, DMS, and H_2S was monitored. The same experiments were performed for bioreactor 2 and 3. Therefore, the average values of MT, DMS, and H_2S production could be determined. All processes mentioned above were repeated when cysteine was replaced by 0.05 mmols. L-methionine (Met), another amino acid containing sulfur in the side chain (Fig. 1).

2.4. Batch methanogen toxicity assay

Two samples (150 mL each) withdrawn from bioreactor 1 were placed in two different serum bottles (300 mL each), once served as a control for the other. A rubber stopper with a gasbag to serve as a gas collector was placed on the top of an individual bottle and tightly sealed to prevent gas leakage and to ensure anaerobic conditions. Mixing was also provided for each bottle. All bottles were kept at a constant temperature (35°C) during the experiments. A 0.15 mmols methanogen inhibitor, ethyl-2-butynote (EB), was added to the bottle that did not serve as a control. MT, DMS, and methane production were daily monitored. The content of methane gas was determined by gas chromatography with flame ionization detection. The same experiments were performed for bioreactor 2 and 3. Therefore, the average values of MT, DMS, and methane production could be determined for evaluation. All chemicals were made up at the appropriate concentration in a phosphate buffer with pH 7.0 so that the addition of 1 mL of solution yielded the above total mass of chemical being added to the bottle. The control sample had 1 mL of phosphate buffer addition [25].

2.5. Analytical methods

The headspace analysis method developed by Novak et al. [17] was used to characterize odor production. The static headspace gas samples were analyzed for odorous gases by gas chromatography, mass spectrometry (GC/MS, GC 5890, MSD 5971, AGILENT, Amphur Muang Rayong, Rayong 21000, Thailand). A volume of 200 μL of gas was injected with a gastight syringe into an on-column inlet connected to a 30 m × 0.32 mm ID × 1 μm column with 95% silicon 5% phenyl (Agilent, Amphur Muang Rayong, Rayong 21000, Thailand), using helium as a carrier gas with a flow of 2 mL/min. Liquid nitrogen was used to cool in a Dewar jar in the first meter to trap the analytical compounds and produce narrow peaks during the injection. Specific odor compounds identified including methanethiol, DMS, DMDS, and hydrogen sulfide.



Cysteine Methionine

Fig. 1. Molecular formulae of (a) cysteine and (b) methionine.

3. Results and discussion

3.1. Generation and fate of VOSC

The data in Fig. 2 display MT, DMS, DMDS, and H_2S profiles generated from anaerobic digestion of WAS in bioreactors 1, 2, and 3. They reflected MT as the major VOSC observed. As shown in the figure, MT concentration increased to a peak value of 275 mg/m^3 after 14 d in the first reactor and 225 mg/m^3 after 22 d in the second and third reactors. After the peak, the MT profile exhibited a continuous decline until almost the end of the monitoring period.

DMS formation occurred simultaneously with MT but at a much slower rate. The DMS profile reached a peak of 175 mg/m^3 in the first reactor and around 150 mg/m^3 in reactors 2 and 3, all at the 34th day of monitoring; then, the profile decreased steadily in a way that its concentration remained always higher than the MT concentration after 30 d of system operation. The H_2S profile displayed a continuous increase throughout the observation period and became the primary sulfur compound at the end of monitoring, with around 400 mg/m^3 in reactor 1 and 230 mg/m^3 in reactors 2 and 3.

The numerical values in Fig. 1 mainly relate to the experimental setup used in the study. The more significant aspect of the data displayed in the figure was the trend showed for the generation and fate of VOSCs. It essentially indicated a very similar pattern for VOS profiles in all three reactors. At the beginning of the monitoring period, the concentration of MT, DMS, and H_2S began to increase; the rate of accumulation was significantly faster for MT as compared to the other compounds. H_2S could be formed directly from the reduction of sulfate under anaerobic condition or directly, from amino acids such as cysteine [26]. Similarly, MT (CH_4S) would be generated from the hydrolysis of both cysteine and methionine:

$$C_3H_7NO_2S + H_2O \rightarrow H_4S + C_2H_5NO_3 \quad (1)$$

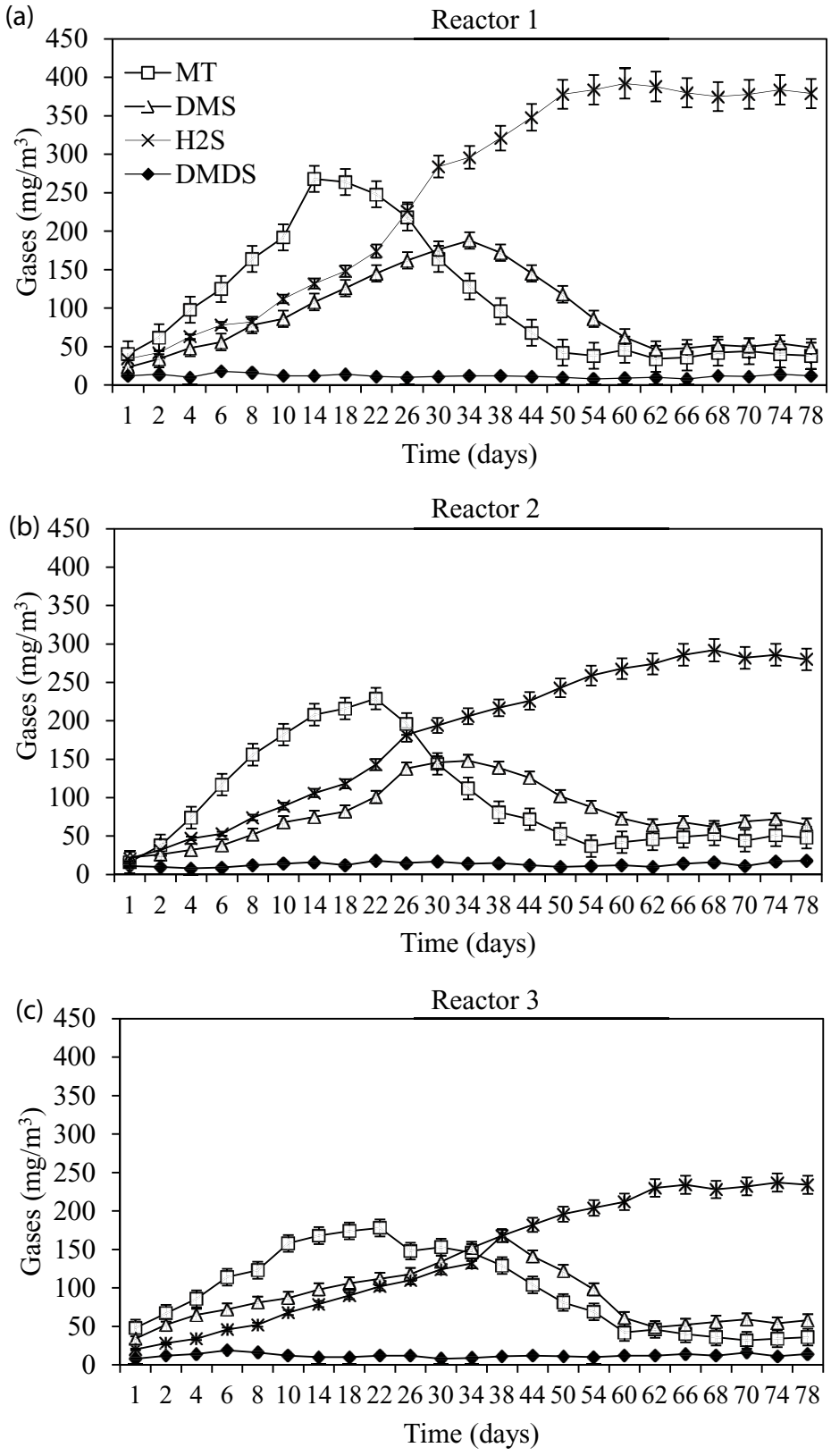


Fig. 2. Pattern of VOSC profiles associated with anaerobic digestion WAS in (a) bioreactor 1, (b) bioreactor 2, and (c) bioreactor 3.

$$C_5H_{11}NO_2S + H_2O \rightarrow CH_4S + C_4H_9NO_3 \quad (2)$$

MT peaked early in the cycle and its decline was usually associated with an increase in DMS, suggesting that DMS was being generated from MT. As also suggested by Higgins et al. [26], MT would undergo methylation with acetic acid, a major volatile fatty acid found under anaerobic conditions to produce DMS (CH_3SCH_3):

$$CH_4S + CH_3COOH \rightarrow CH_3SCH_3 + HCOOH \quad (3)$$

Then, DMS is converted to H_2S through demethylation. The H_2S is the sulfur compound left after the decline of organo-sulfur compounds at the end of the monitoring periods. The decrease of the DMS profile after the 34th day generated additional H_2S. During the whole process, DMDS remained quite low. The results suggested that the degradation of sulfur-containing amino acids, cysteine, and methionine were the primary source of H_2S and MT; the latter was then converted to DMS, DMDS, and finally to H_2S.

3.2. Impact of sulfur-containing amino acids on VOSC generation

Higgins et al. [16] and Forbes et al. [27] have reported the release of significant amounts of cysteine and methionine, the sulfur-containing amino acids, during anaerobic digestion of WAS. Accordingly, this section explored the impact of these two amino acids on VOSC generation, through biodegradation under anaerobic conditions. Fig. 3 displays the enhanced MT profile obtained by the addition of 0.05 mmol of L-cysteine and L-methionine. As shown in the figure, the peak of MT profile is reached between 8 and 9 d of monitoring. The maximum level of MT concentration was 840 and 380 ppm with the addition of methionine and cysteine, respectively. These values corresponded to around 3.4- and 1.5-fold increases with respect to the control bioreactor. Fig. 3 also shows complete biodegradation of MT after 18 d of exposure to anaerobic conditions.

Fig. 4 shows the DMS profiles modified by the addition of the same amino acids, increasing its peak values to 480 and 380 ppm by methionine and cysteine, respectively. A similar increase was also observed for H_2S generation, as indicated in Fig. 5, from around 300 to 310 ppm in the control bioreactor to 600 ppm for cysteine and 1,150 ppm for methionine. It should be noted that the H_2S generation rate was considerably increased after 8–10 d with the decline of MT and DMS profiles.

These results indicate that sulfur amino acids were degraded during the anaerobic digestion of WAS and this degradation generated VOSCs associated with odors. The results also suggest that L-methionine and L-cysteine might potentially be the primary substrates for VOSCs and the production of MT and DMS was possibly due to cleavage at the side chain of methionine and cysteine [28]. The supportive experimental evidence of the results of this study is also provided by Higgins et al. [18] on 10 different anaerobically digested biosolid samples under mesophilic conditions. They measured bound Met and Cys from the proteins in the solution, observing that mass of Met and Cys extracted from biosolids perfectly correlate with MT production during storage. This simply suggests that as the amount of Met and Cys increase, the concentration of MT directly increases. Their results indicate that the degradation of Met and Cys was responsible for the production of VOSCs. The results also imply that the measurement of Met and Cys could be used to determine the possibility of odor production from anaerobic biodegradation of biosolids. However, the measurement of protein alone would not indicate possible levels of Met or Cys concentrations in the protein because some proteins may have more Met and/or Cys than others. Therefore, the amount of protein and Met or Cys would not directly correlate with each other.

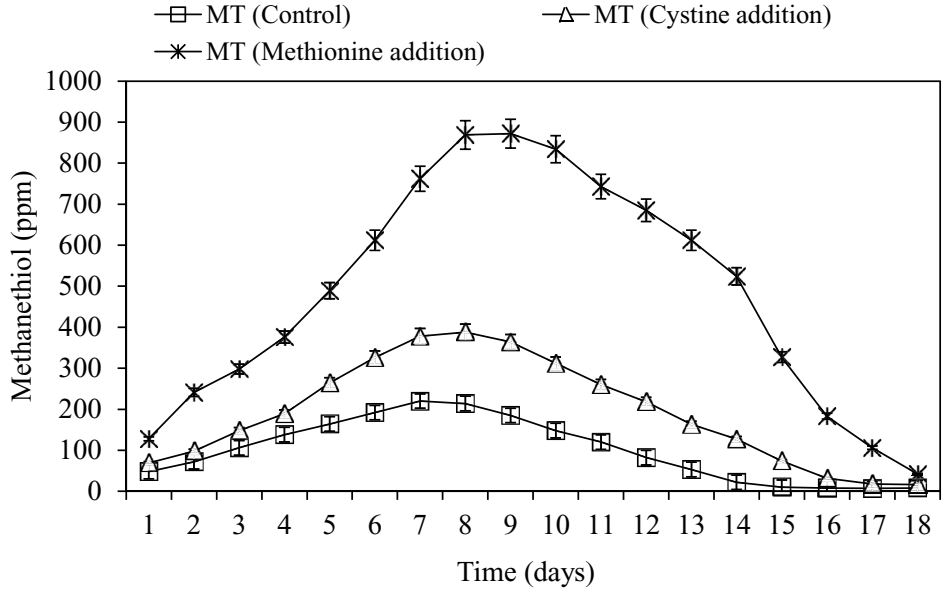


Fig. 3. Impact of methionine and cysteine on MT production.

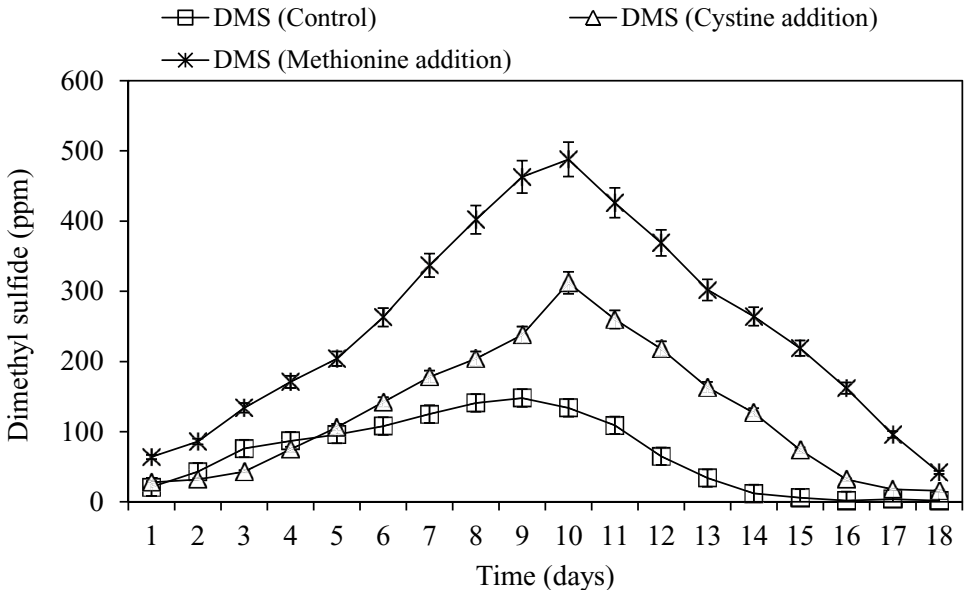


Fig. 4. Impact of methionine and cysteine on DMS production.

3.3. Impact of methanogenic activity on VOSC generation

Several researchers have reported that methanogens were able to utilize and degrade VOSCs such as MT, DMS, and DMDS [21,26,29]. Lomans et al. [30] suggested that a balance could be established between the production and the degradation of VOSCs in the sediment; this resulted in low emission of these compounds if the system was undisturbed. Interestingly, the study from Kelly et al. [28] argued that a similar balance, that is, generation and biodegradation of these compounds, most likely existed in anaerobic digestion of WAS. Zitomer and Speece [29] found that when an anaerobic digester was operated in conditions that induced an inhibitory effect on methanogens such as unusual pH or temperature or exposure to toxic chemicals, methanogenic activity was decreased and simultaneous emission of MT was observed. These results gave the indication that if methanogens were inhibited, MT and/or DMS would accumulate in the bioreactor. Therefore, maintaining good methanogenic activity would remove the odorous VOSCs.

Consequently, this portion of the experiments in this current study tested the role of methanogens on the fate of VOSCs. For this purpose, ethyl-2-butynote (EB), which has an inhibitory impact on methanogenic activity, was added to the bottle that did not serve as the control system. The results are plotted in Figs. 6 and 7. Fig. 6 gives a direct indication of the inhibitory impact of EB on methanogenic activity. While the methane concentration remained at basically the same level in the control bottle during the whole observation period, it dropped to a negligible level after the 18th day of monitoring in the bottle started with the EB dose, indicating a radical reduction in methanogenic activity. Similar trends were also detected in the MT and DMS profiles. As shown in Fig. 7a, the control bottle exhibited a typical MT profile with an initial increase to a peak value of around 200 ppm, followed by a decline and total depletion due to biodegradation. However, in the bottle containing EB, MT concentration sharply increased to 800 ppm (a 4-fold increase) and remained at this level for the rest of the observation period. Likewise, the typical DMS profile was observed in the control bottle, whereas DMS concentration exhibited a steady increase to around 450 ppm under the inhibitory impact of EB (Fig. 7b).

These results confirmed that (i) methanogens play a significant role in the fate of VOSCs; and (ii) a balance exists between the production and degradation of VOSCs when the activity of methanogens is not disturbed. As a result of this balance, VOSC emissions stayed at very low levels or completely stopped. However, inhibition of methanogenic activity induces the accumulation of VOSCs and their subsequent release. Therefore, an odor-causing VOSC such as MT in the digester outlet can be an indicator of inhibition and/or toxicity [31,32].

3.4. The mechanisms of biogas production

The acetoclastic methanogens utilize acetate as a substrate which is a carbon and energy (electron donor) source to generate methyl-tetrahydrosarcinapterin (CH_3–H_4SPT), a significant metabolic intermediate. The methyl group of CH_3–H_4SPT is then transferred to coenzyme M (HS-CoM) to produce methyl-coenzyme M (CH_3–S–CoM). This reaction is catalyzed by CH_3–H_4SPT with coenzyme M methyltransferase (Mtr). Subsequently, the methyl group of methyl-coenzyme M is reduced to methane (CH_4) with coenzyme B (HS-CoB), and Methyl-coenzyme M reductase (Mcr) serving as an electron donor and a catalyst, respectively. In this reaction, heterodisulfide (CoM–S–S–CoB) is another product in which it is further reduced to coenzyme M and coenzyme B available for the next cycles of microbial metabolisms. In contrast, the hydrogenotrophic methanogens oxidize hydrogen (H_2) with carbon dioxide (CO_2) serving as a carbon source to produce methyl-tetrahydromethanopterin (CH_3–H_4MPT), a

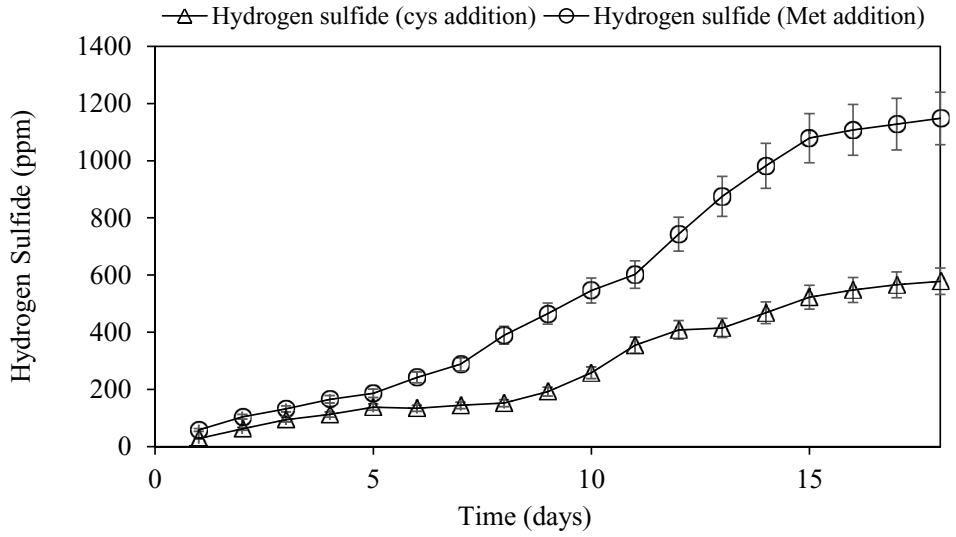


Fig. 5. Impact of methionine and cysteine on H2S generation.

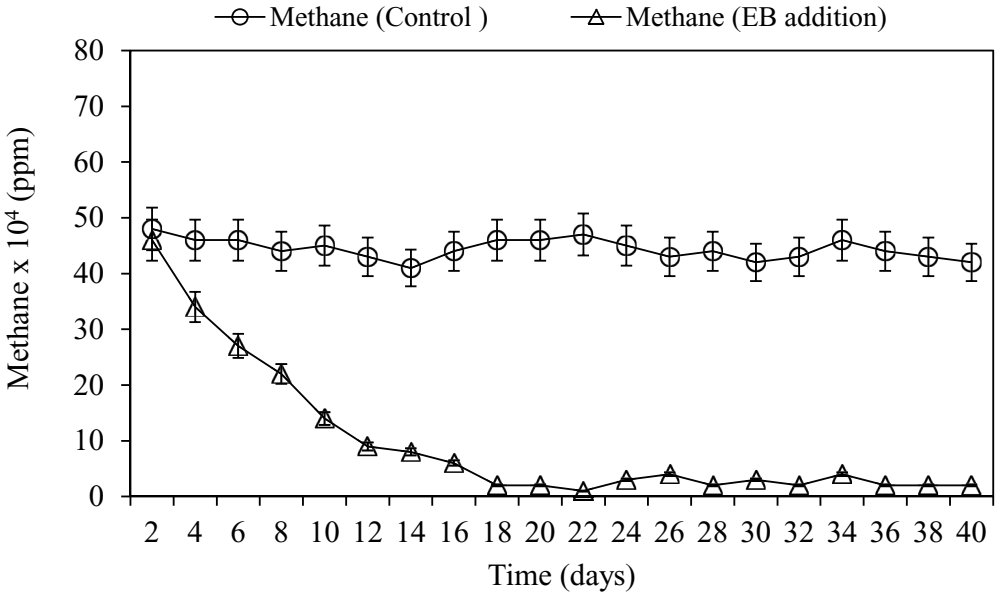


Fig. 6. Effect of ethyl-2-butynote on methane production.

key metabolic intermediate, in lieu of CH_3–H_4SPT. The following reactions are identical to those occurring in acetoclastic methanogens.

The methyl-coenzyme M undergoes reductive methylation in which the methyl group is reduced to methane using the electrons from coenzyme B. Then, all subsequent reactions mentioned above are repeated.

Both hydrogenotrophic and acetoclastic methanogens can utilize methanethiol generated from DMS degradation as a metabolic intermediate. In this case, the methyl group is transferred to coenzyme M, resulting in hydrogen sulfide (H_2S), and methyl-coenzyme M generation. The following reactions for methyl-coenzyme M are identical to those already mentioned.

According to the data in this study and the metabolic pathways for both hydrogenotrophic and acetoclastic methanogens mentioned above, it can be seen that biogases (CH_4 and H_2S) production are most likely to be due primarily to the degradation of VOSCs, DMS, and methanethiol.

4. Conclusion

In light of the experimental results presented above, the conclusive comments of the study may be summarized as follows:

Sulfur-containing amino acids, released through hydrolysis and the breakdown of proteins under anaerobic conditions, serve as the primary organic sources of H_2S and MT

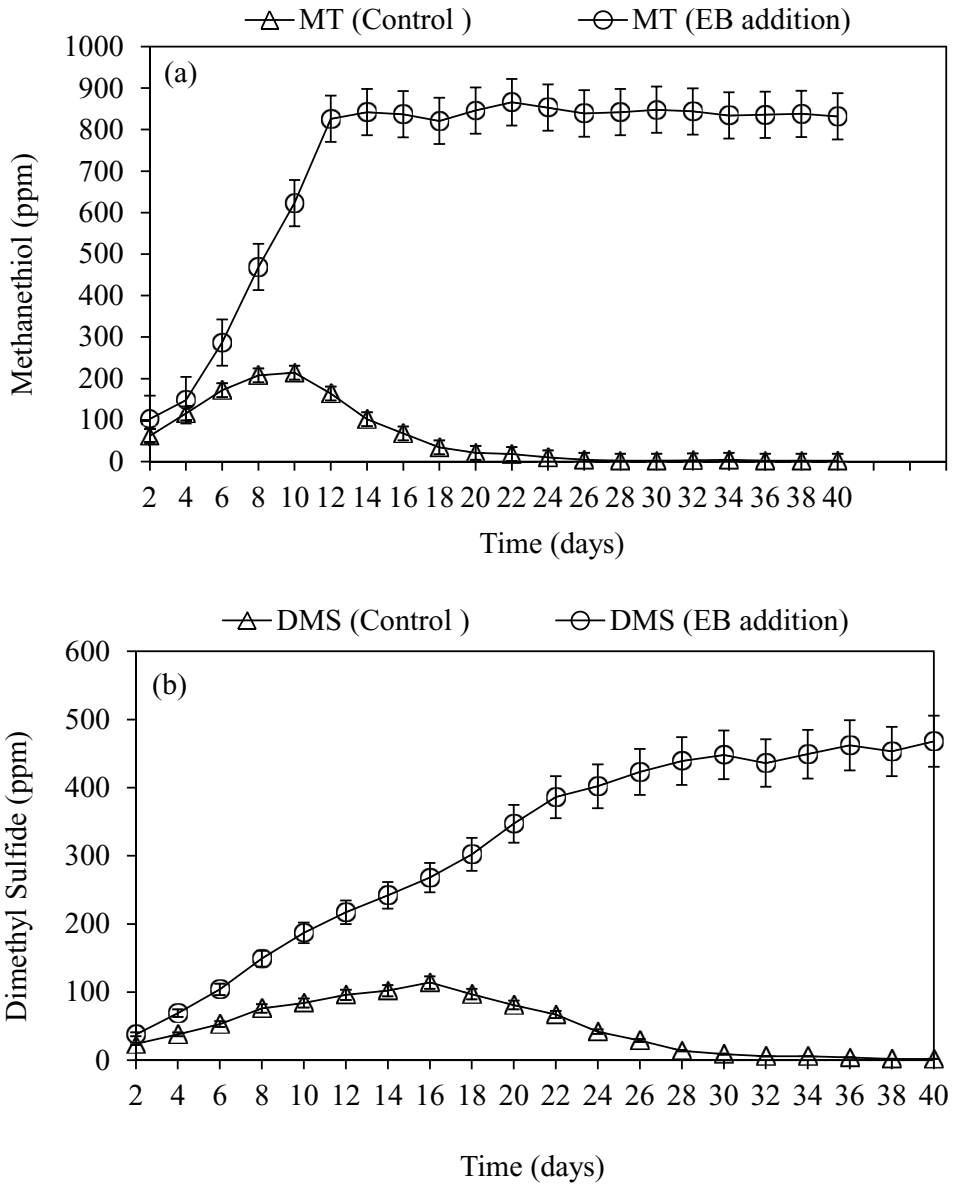


Fig. 7. Effect of ethyl-2-butynote on the production of (a) MT and (b) DMS.

generation. MT is then converted to DMS, DMDS, and finally to H_2S.

The external addition of two amino acids L-cysteine and L-methionine significantly enhances both MT and DMS generation, suggesting that these amino acids might potentially be the primary substrates for VOSCs; the production of MT and DMS is possibly due to cleavage at the side chain of L-methionine and L-cysteine.

Under normal conditions, VOSC profiles exhibit a balance between generation and degradation. Therefore, VOSC could be utilized as a substrate by methanogens, which plays a significant role in the fate of VOSCs.

When the activity of methanogens is not disturbed, the balance between the production and degradation of VOSCs is maintained As a result of this balance, VOSC emissions stay at very low levels or completely stop. However, inhibition of methanogenic activity induces accumulation of VOSCs and their subsequent release.

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