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Original Research

Selection of *in-situ* Desulfurizers for Chicken Manure Biogas and Prediction of Dosage

Hao Jiang[1], Teng Li[1], Walter Stinner[2], Hong Nie[1], Jiangtao Ding[1], Hongjun Zhou[1]*

[1]Institute of New Energy, State Key Laboratory of Heavy Oil Processing, Beijing Key Laboratory of Biogas Upgrading Utilization, China University of Petroleum, Beijing 102249, China
[2]Biochemical Conversion Department, Deutsches Biomasseforschungszentrum gGmbH (DBFZ), Torgauer Straße 116, 04347 Leipzig, Germany

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Abstract

The hydrogen sulfide (H_2S) in biogas is poisonous and corrosive, so it is usually removed in the early stage of biogas upgrading. Dosing iron compounds directly into the anaerobic fermenter is an *in-situ* method for rough desulphurization. But it is difficult to estimate the appropriate amount of iron compound to add and overdosing is usually inevitable. Five kinds of iron compounds ($FeCl_2$, $FeCl_3$, $Fe(OH)_3$, Fe_2O_3, and $FeSO_4$) were applied as *in-situ* desulfurizers in chicken manure fermentation to reduce H_2S emissions. Biogas yield, CH_4 concentration, and H_2S concentration were examined to evaluate the performance of these desulfurizers. Among these five desulfurizers, $FeCl_2$, $FeCl_3$, and $Fe(OH)_3$ showed better performance; the desulfurization rates were all above 98.5% when the addition was 16 mmol L^{-1}. In order to establish the prediction model of the required amount for *in-situ* desulfurizer, it is assumed that the dosage of desulfurizer could be simply divided into two parts: one part for consumption of released H_2S, and the other part for guaranteeing a certain desulfurizing level. Under this assumption, the prediction formulas were fitted based on the bottle experiments and applied in a 5 L fermentation system. The required desulfurization levels (H_2S concentration) when adding $FeCl_2$, $FeCl_3$, and $Fe(OH)_3$ were set to 120, 200, and 100 ppmv, respectively. After adding the calculated dosage of the three *in-situ* desulfurizers, the actual H_2S concentrations were 163.0, 180.3, and 89.4 ppmv, respectively, which were relatively closed to the required desulfurization levels.

Keywords: biogas, desulfurizer, hydrogen sulfide, anaerobic fermentation, dosage

Introduction

Against the backdrop of less fossil fuel and more severe environmental pollution, energy recovery from organic residues is becoming a more attractive proposition. Biogas, produced by microorganisms during anaerobic biomass fermentation, consists primarily of CH_4 (40-75%) and CO_2 (15-60%), as well as H_2S (0.005-2%) and other trace components [1]. After desulphurization and dehydration, biogas can be used to generate heat and electricity. After further upgrading process to increase the concentration

*e-mail: zhouhongjun@cup.edu.cn

of CH_4 and reduce impurities, biogas can be transformed into biomethane and applied as a substitute of natural gas.

The H_2S in biogas is mainly related to the anaerobic degradation of S-containing organic material such as sulfolipid or amino acid, or formatted by sulfate reduction, where sulfate is used as the terminal electron acceptor [2]. The H_2S content depends on the type of organic substrates feeding for fermentation. The fermentation of manure or food waste shows typical H_2S concentrations in the range of 2,000-6,000 ppmv in biogas, while for anaerobic wastewater treatment in the paper industry, H_2S concentration can be measured at up to 30,000 ppmv [3].

H_2S can cause corrosion in pipelines and equipment, along with high toxicity for health and the environment. Therefore, it is usually removed in an early state of the biogas upgrading process. A variety of methods have been used for desulphurization, which can be classified as physical, chemical, and biological methods according to principle, or as *in-situ* and external according to process, or as rough and fine desulphurization according to purification level. The comparative overview of these methods is given elsewhere [1, 4-5]. The method or combination of methods for desulphurization can be determined based on the biogas composition and subsequent utilization.

Dosing iron compounds (especially iron salts) directly into the fermenter is an *in-situ* method for rough desulphurization. This desulphurization method has the advantages of simple operation, small investment, and good desulphurization rate. Five kinds of natural iron ores were used as *in-situ* desulfurizers during the anaerobic digestion of waste-activated sludge, and limonite showed high desulfurization efficiency [6]. Besides being used as H_2S control in anaerobic fermenters, iron compounds have been widely used for the abatement of sulfide-associated problems in sewer systems [7-8]. The reactions among iron and sulfide species in these aqueous phases are complex and have not yet been unequivocally ascertained and quantified [9]. Under the most common description, the main desulphurization interactions occurring in anaerobic fermenters are shown in Equations 1 and 2 [1, 9]. Fe (II) can remove sulfide by forming ferrous sulfide precipitation. Fe (III) can remove sulfide by oxidizing it to sulfur while being reduced to Fe (II), which can subsequently produce ferrous sulfide.

$$Fe^{2+} + HS^- \rightarrow FeS + H^+ \quad (1)$$

$$2Fe^{3+} + HS^- \rightarrow 2Fe^{2+} + S + H^+ \quad (2)$$

The achievable desulfurizing level of this method is about 100-150 ppmv [1], but it is difficult to estimate the appropriate adding amount of iron compound and the practical application relies heavily on empirical experience. For the assurance of desulphurization effect, overdosing is usually necessary, which not only increases operational cost, but also poses a potential pollution risk. In addition, too much iron compound could reduce the availability of necessary nutrients like phosphate and sulfur.

In this study, different iron compounds, including $FeCl_2$, $FeCl_3$, $Fe(OH)_3$, Fe_2O_3, and $FeSO_4$, were applied as *in-situ* desulfurizers in chicken manure (CM) fermentation to reduce the emission of H_2S. The biogas yield, CH_4 concentration, and H_2S concentration were examined to evaluate the performance of these desulfurizers. In order to establish the prediction model of the required amount for *in-situ* desulfurizer, it is assumed that the dosage of a desulfurizer could simply be divided into two parts, one part for consumption of released H_2S and the other part for guaranteeing a certain desulfurizing level. Under this assumption, the prediction formulas were fitted and applied successfully in a larger fermentation system.

Materials and Methods

Substrates and Inoculum

Two batches of fresh CM were successively collected from a chicken farm (DQY Ecological Farm, Beijing, China), labeled CM1 and CM2, respectively. The total solids (TS) and volatile solids (VS) were determined to be 29.1% (based on fresh mass) and 68.0% (based on TS) for CM1, and 30.7% and 35.1% for CM2. The digested effluent of the biogas plant feeding CM on the farm was used as inoculum. The TS of the inoculum was below 1%, so the contribution of inoculum to solid content was ignored in calculation.

Fermentation and *in-situ* Desulfurization

The batch fermentation of CM and *in-situ* desulfurization were taken in two kinds of apparatuses: 50 mL bottles and 5 L fermenters (BIOTECH-5JG-2, Baoxing Bio-Engineering Equipment Company, Shanghai, China). For all fermentation, the inoculum took 35% of the loading volume, and the initial TS content was adjusted to 7.0% through mixing CM, inoculum, and water. The bottles were loaded with 25 mL feed mixture and incubated at 37ºC and 130 r min^{-1}. Five kinds of iron compounds ($FeCl_2$, $FeCl_3$, $Fe(OH)_3$, Fe_2O_3 and $FeSO_4$) were added into bottles as *in-situ* desulfurizers with the feedstock, respectively. For each iron compound, different initial concentrations based on the fermentation volume were applied, which were 0 (as a control), 2, 4, 8, 12, 16, and 32 mmol L^{-1}, respectively. In 5 L fermenters, the feeding volume was 3.5 L. The temperature was kept at 37ºC and the stirring rate was 100 r min^{-1}. CM1 was the feedstock in bottles except that when $Fe(OH)_3$ was applied as the desulfurizer, while CM2 was fed in 5 L fermenters as well as bottles adding $Fe(OH)_3$.

Prediction Model of Desulfurizer Dosage

The dosage of desulfurizers was assumed to be divided into two parts: one for consumption of released H_2S and the other for guaranteeing a certain desulfurizing level. It was calculated by Equation 3:

$$m = m_r + xV \quad (3)$$

…where m is the dosage of desulfurizer; m_r represents the amount of desulfurizer that reacted with reduced H_2S, whereas the reduced H_2S can be calculated by subtracting the expected value of H_2S from the H_2S yield without desulfurizer added; x represents the needed concentration of desulfurizer maintained in the liquid for achieving a specific H_2S value in biogas; and V is the fermentation volume. The relationship between H_2S concentration in biogas and desulfurizer concentration in liquid (x) can be obtained by fitting experimental data during the middle period of the 50 mL fermentation.

Analytical Methods

TS and VS were determined according to the standard methods [10]. For 50 mL bottles, pH was measured using a pH meter (PHSJ-4A, REX Instrument Company, Shanghai, China), and biogas yield was determined by 100 mL syringe. For 5 L fermenters, pH was recorded automatically, and biogas yield was determined by the gas-collecting method of draining saturated $NaHCO_3$. The concentration of CH_4 was analyzed by gas chromatography (GC) with a thermal conductivity detector (TCD) (Model GC-2000III, Shanghai Institute of Computing Technology, China) and a packed TDX-01 column using H_2 as the carrier gas. The temperatures of the injector, column, and TCD were 150, 120, and 250ºC, respectively. The concentration of H_2S was analyzed by GC (Agilent 7890A, Agilent Technologies, USA) with a sulfur chemiluminescence detector (SCD) using a capillary column GS-GASPRO (60 m×0.32 mm), and the carrier gas was He. The initial temperature of the column was 60ºC for three minutes. Then the column was heated to 200ºC at a rate of 10ºC min^{-1}, and finally kept for 15 minutes. The temperatures of the injector, SCD, and burner were 250, 250, and 800ºC, respectively.

Results and Discussion

Selection of *in-situ* Desulfurizers

Five iron compounds ($FeCl_2$, $FeCl_3$, $Fe(OH)_3$, Fe_2O_3 and $FeSO_4$) were applied as *in-situ* desulfurizers with different concentrations in 50 mL bottles. The characteristics of biogas production were shown in Fig. 1. Compared with the controls, the biogas yield and CH_4 concentration of the CM fermentation with desulfurizers showed no obvious differences, indicating that adding iron compounds did not cause significant inhibition or promotion to the biogas production. Iron is an essential trace element that is required by methanogens and other microorganisms during fermentation for electron transport and function of certain enzymes [11]. The optimum iron concentration was reported to range from 0.28 to 50.4 g m^{-3} [12]. Some studies have proven that adding iron could provide more biogas production and CH_4 content, especially in the mono-fermentation of agricultural crops, which suffers from a lack of trace elements easily [13-14]. But there are seldom reports about the deficiency of trace elements in CM fermentation, and in fact feeding with animal excrement can generally satisfy the demand for micronutrients [11]. Therefore, adding iron compounds had no significant influence on biogas production in this study. Zhou et al. found that adding limonite had different impacts on biogas production with different initial concentrations of sulfate, which might be due to the changes of microbial quantity and activity under different conditions [6].

The desulfurization rates of different desulfurizers at different concentrations are listed in Table 1. Combined with the H_2S concentration changes in Fig. 1, it clear that the H_2S content decreased obviously after adding desulfurizers. For each kind of iron compound, the more amounts added, the less H_2S was obtained. Among these five *in-situ* desulfurizers, $FeCl_2$, $FeCl_3$ and $Fe(OH)_3$ showed better performance; the desulfurization rates were all above 98.5% when the addition was 16 mmol L^{-1}. Considering avoiding the introduction of other potentially polluting ions, $Fe(OH)_3$ was more environmentally friendly. Compared with the three desulfurizers mentioned above, the desulfurization efficiency of Fe_2O_3 was much lower, and when the addition was 16 mmol L^{-1}, the desulfurization rate was only 90.5%. Due to its insolubility in water, Fe_2O_3 could not fully contact and react with H_2S. So it is not a good choice as an *in-situ* desulfurizer. When $FeSO_4$ was applied, the desulfurization effect seemed normal in the early stage of fermentation, but later the H_2S concentration increased sharply – far higher than that of control (up to 9,000 ppmv). This indicated that the added SO_4^{2-} got involved in the microbial reaction process, employed by sulfate-reducing bacteria as an electron acceptor to generate H_2S [6, 15]. Therefore, $FeSO_4$ was not suitable for *in-situ* desulfurization use. In the following model calculation and experiments, the three desulfurizers with good performance ($FeCl_2$, $FeCl_3$ and $Fe(OH)_3$) were applied.

Prediction Model of Desulfurizer Dosage

To determine the dosage of desulfurizer is key for the *in-situ* desulfurization process. But until now, there has been no public report about how to determine the desulfurizer addition. We supposed that the H_2S concentration was associated with the concentration of the desulfurizer in fermentation liquid. Through the experiments in 50 mL bottles, the fitted curve between the desulfurizer concentration in liquid and the H_2S concentration in biogas was acquired (Fig. 2). The fitting formula was shown as Equation 4 and the values of R^2 were all above 0.999.

$$y = (a + bx^c)^{-1} \quad (4)$$

…where x represents the desulfurizer content in the liquid and y represents the H_2S content in biogas. For $FeCl_2$, the values of a, b, and c were -5.09×10^{-4}, 0.0016, and

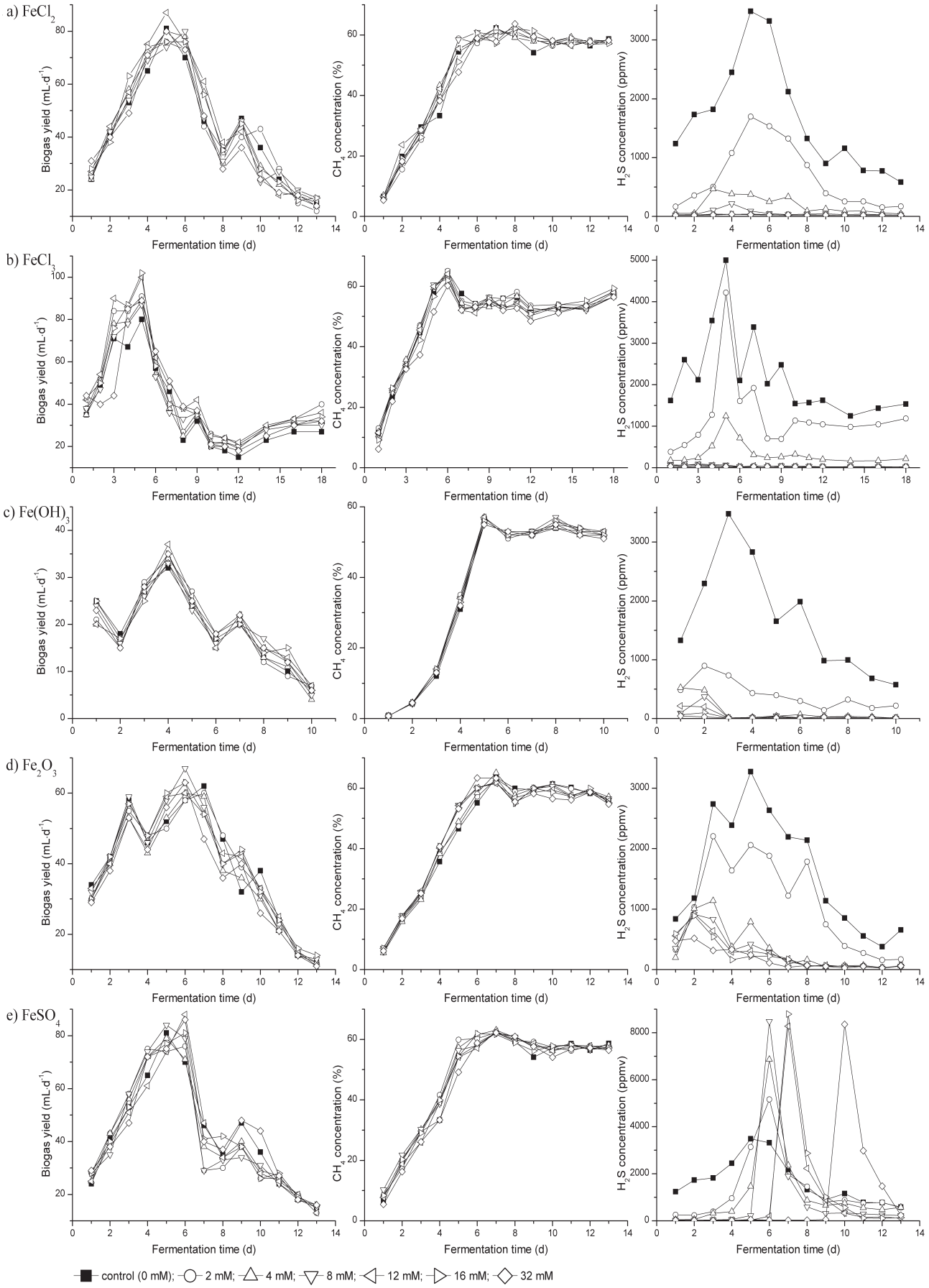

Fig. 1. Biogas yield, CH_4 concentration, and H_2S concentration when using a) $FeCl_2$, b) $FeCl_3$, c) $Fe(OH)_3$, d) Fe_2O_3, and e) $FeSO_4$ as *in-situ* desulfurizers with different concentrations in 50 mL bottles.

Table 1. Desulfurization rates of different desulfurizers at different concentrations.

Concentration of desulfurizer (mmol L^{-1})	Desulphurization rate (%)				
	$FeCl_2$	$FeCl_3$	$Fe(OH)_3$	Fe_2O_3	$FeSO_4$
2	57.3	34.5	77.4	32.5	18.1
4	87.7	81.9	93.9	79.7	25.2
8	96.4	97.9	97.0	82.7	29.0
12	98.6	98.1	97.4	84.2	52.6
16	98.5	98.6	98.7	86.1	51.6
32	98.9	99.0	99.1	90.5	56.7

1.171, respectively; for $FeCl_3$ the values of *a*, *b*, and *c* were 2.295×10^{-4}, 1.504×10^{-4}, and 2.561, respectively; for $Fe(OH)_3$, the values of *a*, *b*, and *c* were 0.1572, -0.1777, and -0.2731, respectively. In fact, the form of Equation 4 is not unchangeable and could be replaced by other forms, as long as it reflects the relationship between *x* and *y* in the concentration range of desulfurizer.

For example, when $FeCl_2$ was used as the *in-situ* desulfurizer, if the required H_2S content in biogas was 200-300 ppmv, according to Equation 4, the $FeCl_2$ concentration in liquid should maintain around 2.11-2.87 mmol L^{-1}; if the required H_2S content in biogas was 50 ppmv, the $FeCl_2$ concentration in liquid should be 8.83 mmol L^{-1}. It also can be seen from Fig. 2 that with the increase of desulfurization level, much more addition of desulfurizer would be needed, and the H_2S content in the biogas could not be reduced unboundedly. In practical application, it is necessary to consider the trade-off between desulfurization level and desulfurizer cost. If necessary, this *in-situ* desulfurization method can combine with a fine desulfurization process to obtain a higher desulfurization rate economically.

Through Equations 3 and 4, for a certain required H_2S concentration, the additional quantity of *in-situ* desulfurizer can be calculated.

Application of Prediction Model in 5 L Fermentation

The prediction model was applied in 5 L fermenters. Firstly, the control fermentation without desulfurizer was performed, and the amount of H_2S was recorded. In this experiment, the H_2S concentrations in biogas were assumed to be demanded below 120, 200, and 100 ppmv when $FeCl_2$, $FeCl_3$, and $Fe(OH)_3$ were added as *in-situ* desulfurizers, respectively. Then m_r can be calculated, and *x* can be obtained through Equation 4. Dosage *m* was determined by Equation 3. Table 2 lists the calculated dosage of the three *in-situ* desulfurizers, as well as the actual desulfurization efficiency after adding them. Furthermore, the changes of biogas yield, CH_4 concentration, and pH are shown in Fig. 3; the changes of H_2S concentration are shown in Fig. 4. Consistent with the results in bottles, adding desulfurizers did not promote or restrict biogas or methane production in 5 L fermentation, although the pH values were slightly lower than the control, especially in the fermenter with $FeCl_3$. In Fig. 3 (c), the pH decreased from 7.4 to 6.2 quickly in the first three or four days, corresponding the hydrolysis and acidogenesis stages with acid accumulated in anaerobic fermentation, and then it rose slowly to about

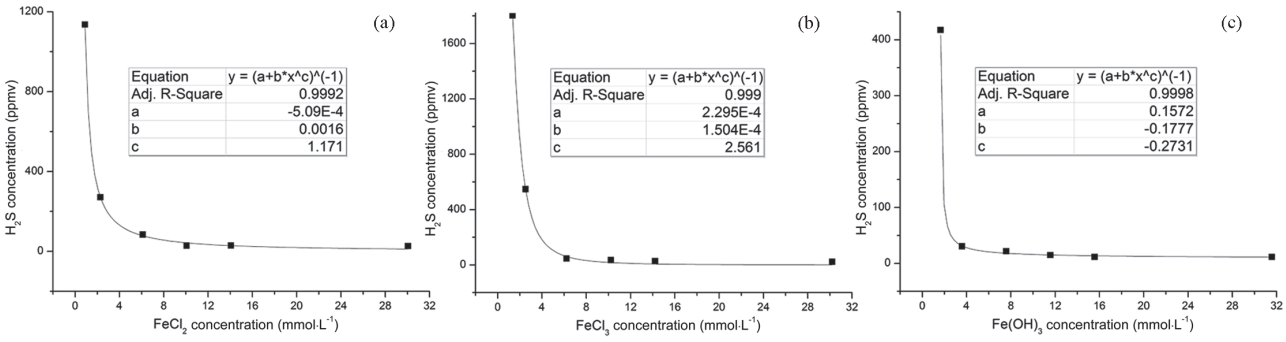

Fig. 2. Correlation curve and equation of desulfurizer concentration in liquid and H_2S concentration in biogas.

Table 2. Addition amounts of $FeCl_2$, $FeCl_3$, and $Fe(OH)_3$ under different desulfurization requirements, and actual desulfurization efficiency.

In-situ desulfurizer	Required H_2S concentration (ppmv)	Dosage prediction			Experiment results	
		x (mmol L^{-1})	m_r (mmol)	*m* (mmol)	Actual H_2S concentration (ppmv)	Desulfurization rate (%)
$FeCl_2$	≤120	4.31	2.50	17.59	163.0	92.6
$FeCl_3$	≤200	3.86	1.60	15.11	180.3	91.8
$Fe(OH)_3$	≤100	1.99	1.68	8.65	89.4	95.8

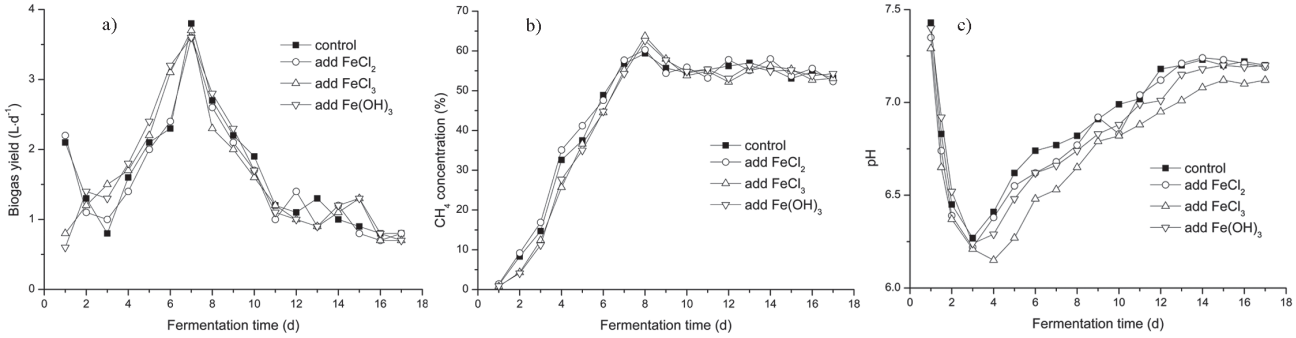

Fig. 3. Changes of biogas yields, CH_4 concentrations, and pH when using $FeCl_2$, $FeCl_3$, and $Fe(OH)_3$ as *in-situ* desulfurizers in 5 L fermenters. The control is no desulfurizer added.

7.2, demonstrating the subsequent methanogenesis stage. Fig. 4 indicates that the production of H_2S also mainly occurred during hydrolysis and acidogenesis stages, and the H_2S content of the control went up to 4918.4 ppmv on the fourth day of fermentation. In the fermenters adding *in-situ* desulfurizers, the peak contents of H_2S ranged from 200 to 600 ppmv. The average H_2S concentrations of 5 L fermentation are given in Table 2. When $FeCl_2$ was used as desulfurizer, the actual H_2S concentration was 163.0 ppmv, which was worse than required (120 ppmv), but still relatively close. When $FeCl_3$ and $Fe(OH)_3$ were applied, the H_2S concentrations in biogas were 180.3 and 89.4 ppmv, respectively, which were close to the required desulfurization level (200 and 100 ppmv), and even a little better. From bottles to fermenters, the working volume increased by 140 times, and the prediction model showed good adaptability and effectiveness.

In the microscopic mechanism, a process of *in-situ* desulfurization will include the competition and collaboration of microorganisms, reactions of sulfur and iron, etc. [6, 16]. But for the prediction of desulfurizer dosage, this simple and practical method can be applied regardless of the complex principles. The calculated dosage should be adjusted flexibly based on the real operation. And according to the actual situations, the experiments for dosage prediction can change the scale, reactor type, batch or continuous feed, etc.

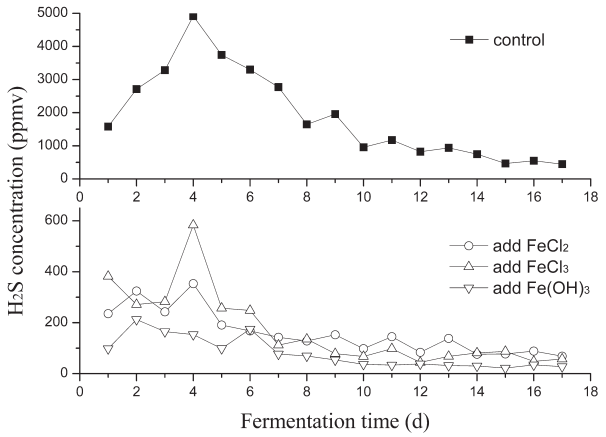

Fig. 4. Changes of H_2S concentrations when using $FeCl_2$, $FeCl_3$, and $Fe(OH)_3$ as *in-situ* desulfurizers in 5 L fermenters. The control is no desulfurizer added.

In this study, two batches of CM were used, and the VS of CM2 was much lower than CM1 due to the high sand content. For the experiments of adding $FeCl_2$ and $FeCl_3$, CM1 was fed in bottles, while CM2 was fed in 5 L fermenters. But the prediction formulas calculated through bottle experiments were applied well in 5 L fermentation, indicating that the prediction models were not sensitive to the property fluctuation of CM. In a follow-up study, the influence of the substrate change to the prediction model should be evaluated in detail, and the adaptability of this method to other substrates also needs to be tested.

Conclusion

How to accurately determine the dosage of added desulfurizer is a key question to *in-situ* desulfurization. In this study, three iron compounds ($FeCl_2$, $FeCl_3$ and $Fe(OH)_3$) were selected as good-performing *in-situ* desulfurizers for CM fermentation, and used in the modeling experiments. For the establishment of the prediction model, regardless of the complex reactions, the dosage of desulfurizer was simply divided into two parts: one part for consumption of released H_2S and the other part for guaranteeing a certain desulfurizing level. With this idea, the prediction formulas were fitted and applied successfully in a 5 L fermentation system. To our knowledge, it is the first time that the prediction method for an *in-situ* desulfurizer dosage has been proposed. The method could be verified and improved through more experiments in laboratory, and practices in actual biogas plants.

Acknowledgments

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References

1. RYCKEBOSCH E., DROUILLON M., VERVAEREN H. Techniques for transformation of biogas to biomethane. Biomass Bioenergy **35**, 1633, **2011**.
2. ANDERSSON F.A.T., KARLSSON A., SVENSSON B.H., EJLERTSSON J. Occurrence and abatement of volatile sulfur compounds during biogas production. J. Air Waste Manage. Assoc. **54**, 855, **2004**.
3. SCHIEDER D., QUICKER P., SCHNEIDER R., WINTER H., PRECHTL S., FAULSTICH M. Microbiological removal of hydrogen sulfide from biogas by means of a separate biofilter system: experience with technical operation. Water Sci. Technol. **48**, 209, **2003**.
4. WEITHÄUSER M., SCHOLWIN F., FISCHER E.R., GROPE J., WEIDELE T., GATTERMANN H. Gas processing and options for utilisation. In *Guide to Biogas-From production to use*; Fachagentur Nachwachsende Rohstoffe e. V. (FNR): Gülzow, 115-140, **2010**.
5. ABATZOGLOU N., BOIVIN S. A review of biogas purification processes. Biofuels, Bioprod. Biorefin. **3**, 42, **2009**.
6. ZHOU Q., JIANG X., LI X., JIANG W. The control of H_2S in biogas using iron ores as in situ desulfurizers during anaerobic digestion process. Appl. Microbiol. Biotechnol. **100**, 8179, **2016**.
7. ZHANG L., KELLER J., YUAN Z. Inhibition of sulfate-reducing and methanogenic activities of anaerobic sewer biofilms by ferric iron dosing. Water Res. **43**, 4123, **2009**.
8. SUN J., PIKAAR L., SHARMA K.R., KELLER J., YUAN Z. Feasibility of sulfide control in sewers by reuse of iron rich drinking water treatment sludge. Water Res. **71**, 150, **2015**.
9. FIRER D., FRIEDLER E., LAHAV O. Control of sulfide in sewer systems by dosage of iron salts: comparison between theoretical and experimental results, and practical implications. Sci. Total Environ. **392**, 145, **2008**.
10. APHA. Solids. In *Standard Methods for the Examination of Water and Wastewater*, 20th ed; American Public Health Association: Washington, D.C., 2540, **1998**.
11. FRIEHE J., WEILAND P., SCHATTAUER A. Fundamentals of anaerobic digestion. In *Guide to Biogas-From production to use*; Fachagentur Nachwachsende Rohstoffe e. V. (FNR): Gülzow, 21-31, **2010**.
12. TAKASHIMA M., SPEECE R., PARKIN G.F. Mineral requirements for methane fermentation. Crit. Rev. Env. Sci. Tec. **19**, 465, **1990**.
13. DEMIREL B., SCHERER P. Trace element requirements of agricultural biogas digesters during biological conversion of renewable biomass to methane. Biomass Bioenergy **35**, 992, **2011**.
14. CASALS E., BARRENA R., GARCÍA A., GONZÁLEZ E., DELGADO L., BUSQUETS-FITÉ M., FONT X., ARBIOL J., GLATZEL P., KVASHNINA K. Programmed iron oxide nanoparticles disintegration in anaerobic digesters boosts biogas production. Small **10**, 2801, **2014**.
15. JING Z., HU Y., NIU Q., LIU Y., LI Y.Y., WANG X.C. UASB performance and electron competition between methane-producing archaea and sulfate-reducing bacteria in treating sulfate-rich wastewater containing ethanol and acetate. Bioresour. Technol. **137**, 349, **2013**.
16. YANG S.L., TANG Y.Q., GOU M., JIANG X. Effect of sulfate addition on methane production and sulfate reduction in a mesophilic acetate-fed anaerobic reactor. Appl. Microbiol. Biotechnol. **99**, 3269, **2015**.