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# Feeding controls H<sub>2</sub>S production in situ in high solid anaerobic digestion

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## Abstract

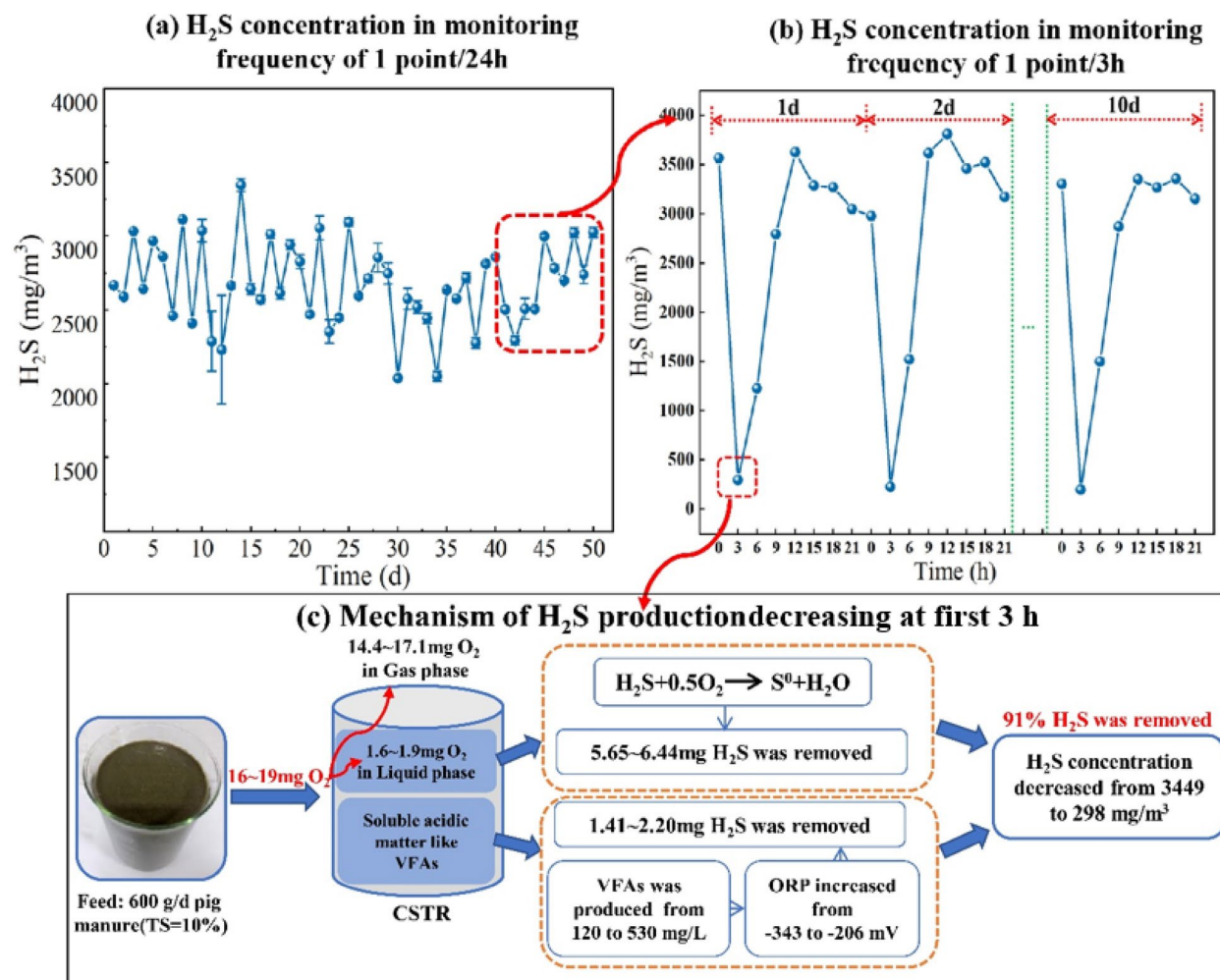
In this study, a high frequency monitoring method was used to assess how semi-continuous feeding affects H<sub>2</sub>S production in high solid anaerobic digestion. The results showed that H<sub>2</sub>S characteristics at a monitoring frequency of 1 point/3 h were different to that of 1 point/24 h, its concentration decreased from  $3449 \pm 227$  mg/m<sup>3</sup> at 0 h to  $298 \pm 45$  mg/m<sup>3</sup> at 3 h. H<sub>2</sub>S concentration was negatively correlated with volatile fatty acids (VFAs), and oxidation reduction potential (ORP). 72–82% of H<sub>2</sub>S reduction in the first 3 h resulted from the introduction of O<sub>2</sub> during feeding, and 18–28% of that was closely related to the production of a large quantity of soluble acidic matter, such as VFAs. A more accurate H<sub>2</sub>S release model was established according to the content of VFAs. Totally, this study implies that feed carrying air is a promising method for in situ control of H<sub>2</sub>S production in anaerobic digestion.

**Keywords:** High solid, Anaerobic digestion, Short time-scale, H<sub>2</sub>S release, Volatile fatty acid

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## Graphical Abstract



## Introduction

Annual livestock and animal manure production in China can reach  $3.8 \times 10^9$  t, with pig manure accounting for 47% of this total ( $\sim 1.8 \times 10^9$  t) (Liu et al. 2020). This large quantity of manure production results in serious environmental pollution. Anaerobic digestion (AD) can transform organic matter into energy and organic fertilizer, thereby achieving a reduction in waste and resource recovery that is of minimal environmental harm (Wafi et al. 2019; Adrover et al. 2020). Given these advantages, this technology has been widely used globally (Li et al. 2014; Hailu et al. 2020). AD is the main technology used within the treatment of animal manure (Tayibi et al. 2021; Wu et al. 2022). Research into anaerobic digestion of waste with a high solid content [total solids (TS)  $\geq 10\%$ ] has become increasingly

popular and further development of this technology in recent years has made it suitable for treating organic fertilizer wastes, such as animal manure, kitchen waste, and agricultural straw (Krishania et al. 2013; Ting et al. 2020; Mertins et al. 2022).

$H_2S$  gas is a product of AD and is poisonous, acidic, and malodorous. This gas also has a strong corrosive effect on pipelines, combustion chambers, and instruments (Oliveros-Muñoz et al. 2021). Therefore, measures must be taken to reduce the concentration of  $H_2S$  gas in the biogas before using the biogas. Previous studies have proved that adding a small amount of  $O_2$  or air can effectively remove  $H_2S$  in the anaerobic digestion system (Diaz et al. 2010; Lim et al. 2014; Yang et al. 2020). Diaz et al. used municipal sludge as raw material, and by supplying  $O_2$  to the anaerobic reactor, the

removal rate of  $\text{H}_2\text{S}$  in biogas can reach about 98%. In CSTR project operation, semi-continuous feed is used and the feed often brings in trace amounts of air; however, no study has been done on how semi-continuous feed affects the production of  $\text{H}_2\text{S}$ .

$\text{H}_2\text{S}$  is mainly derived from the transformation of different forms of sulfur during AD, including sulfate reduction and decomposition of sulfur-containing protein (Yan et al. 2018). Some scholars have studied the release of  $\text{H}_2\text{S}$  during AD. For example, Tian et al. (2020) showed that the average  $\text{H}_2\text{S}$  concentration and production potential in a sequential batch AD test of food waste with 4.2% TS content under a monitoring frequency of 1 point /24 h were  $1065 \pm 267$  ppm and  $765 \pm 163$  g/t (TS), respectively. Yang and Deng (2020) found the  $\text{H}_2\text{S}$  concentration to be  $336 \pm 150$  ppm in semi-continuous AD of pig manure with a TS of 6% under a monitoring frequency of 1 point /24 h. Dai et al. (2017) showed that  $\text{H}_2\text{S}$  concentration and production potential during the AD of activated sludge were  $95 \pm 13$  ppm and  $314.6 \times 10^{-4}$  mL /g volatile solids (VS), respectively, under a monitoring frequency of 1 point /24 h. In general, these studies mainly focused on the emission characteristics of  $\text{H}_2\text{S}$  under a low TS and long-time scale, such as a monitoring frequency of 24 h. In contrast, few studies have focused on the continuity of  $\text{H}_2\text{S}$  production under a high solid content and AD over a short time scale.

Therefore, this study is the first to use a high frequency monitoring method to investigate how semi-continuous feeding affects  $\text{H}_2\text{S}$  production in AD. The method of high frequency detection of 1 point/3 h was used to explore the relationship between the production characteristics of  $\text{H}_2\text{S}$  and  $\text{CH}_4$  and physical and chemical factors in a high-solids Continuous Stirring Tank Reactor (CSTR) process.

## Materials and methods

### Materials

The pig manure used in the present study was obtained from the Chang Ping pig farm in Yuqing County, Guizhou Province, China. The inoculum was extracted from an AD test of pig manure in the laboratory. Table 1 shows the basic characteristics of pig manure and inoculum used in the present study.

### Experimental design

The CSTR reactor was cylindrical (Fig. 1) with a volume of 12 L, an effective volume of 9 L, and a Hydraulic Retention Time of 15 days. The CSTR was operated at a temperature of 35 °C. Semi-continuous feeding was used, 600 mL pig manure (TS=10%) was poured into CSTR in 3 min each day. Monitoring of  $\text{H}_2\text{S}$ ,  $\text{CH}_4$ , and volatile fatty acids was initiated at the start of the reactor.

**Table 1** Basic characteristics of pig manure and inoculum used in the present study

Items	Swine manure	Inoculum
pH	$7.09 \pm 0.00$	$8.19 \pm 0.00$
Total solid content (%)	$38.31 \pm 0.25$	$9.43 \pm 0.58$
Volatile solid content (%)	$79.85 \pm 0.17$	$66.43 \pm 0.32$
Volatile fatty acid (mg/L)	$2345 \pm 184$	–
Total sulfur (mg/L)	$695 \pm 25$	–
S-sulfate (mg/L)	$36.5 \pm 0.4$	–
S-total sulfide (mg/L)	$252.9 \pm 5.7$	–
S-soluble sulfide (mg/L)	$6.1 \pm 0.7$	–

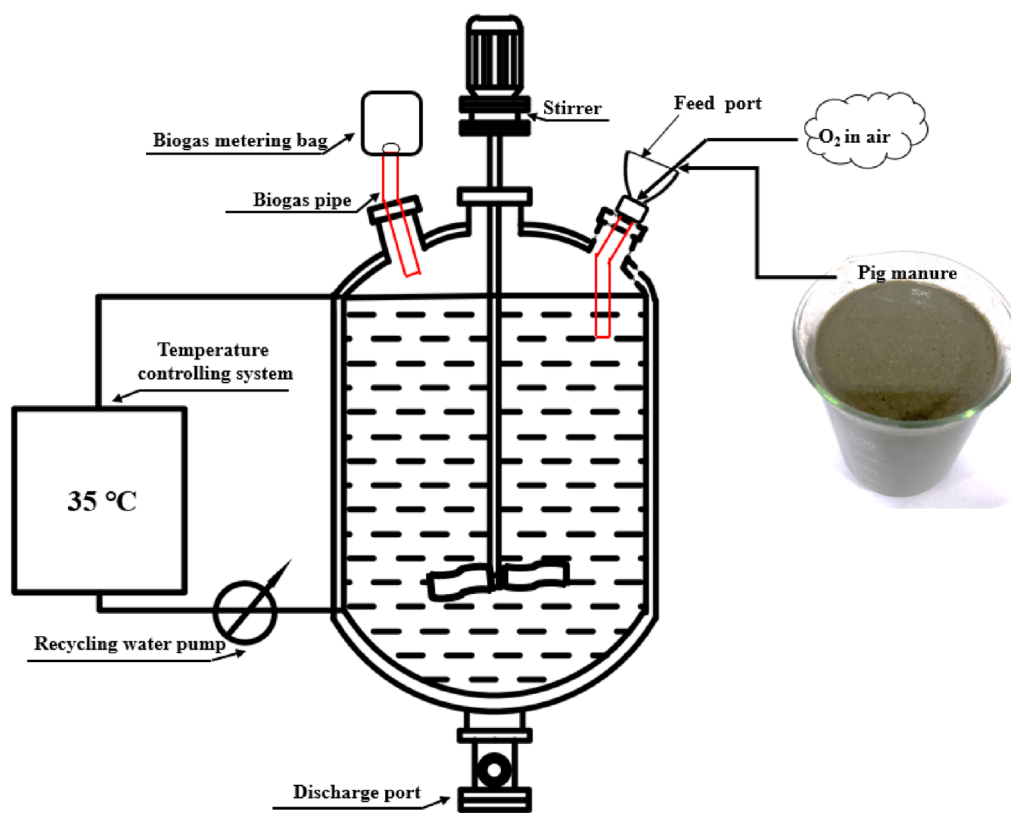
– There is no test

Samples of gas and fermentation broth were collected daily at 0 h (before feeding) and at 3, 6, 9, 12, 15, 18, and 21 h (after feeding). Biogas collected using a tin foil air bag was used for the determination of  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ , and  $\text{O}_2$ . The samples were evenly transferred into a 50 mL sterile tube and stored at  $-25$  °C for the determination of physical and chemical properties.

### Analytical methods

The concentration of  $\text{H}_2\text{S}$  in biogas was determined by gas chromatography (GC 1120, Shanghai Hengping). Injection method: 5 mL of biogas sample containing  $\text{H}_2\text{S}$  was injected into the injection port with a syringe, and the injection volume was controlled to 0.5 mL by the quantification ring in the chromatograph. Operating conditions of the chromatograph: the column was a capillary column (SH-Rtx-1,60 m  $\times$  0.53 mm  $\times$  0.5  $\mu\text{m}$ ), the detector was a Flame Photometric Detector (FPD), the temperatures of the column, the inlet and the detector were 60, 200 and 250 °C, respectively. Helium was used as the carrier gas. Calculation method: The concentration of  $\text{H}_2\text{S}$  in biogas is calculated according to area external standard method.

The daily output of biogas was measured using an LMP-1 wet type anticorrosive gas flow meter (Chongqing Jieheng Peristaltic Pump Co., Ltd.). Measurements of  $\text{CH}_4$  and  $\text{O}_2$  were conducted using a gas chromatograph under the thermal conductivity detector (TCD) method. TS and VS were determined using the gravimetric method (Choudhury and Lansing 2020). pH, oxidation reduction potential (ORP), and dissolved oxygen (DO) were measured using a Hach water quality monitor. Ammonium nitrogen ( $\text{NH}_4^+ - \text{N}$ ) was determined using the Nessler's reagent colorimetric method. VFAs were determined by gas chromatography [gas chromatograph + flame-ionization detection (FID) + DWAX capillary column]. Sulfate and total sulfur content were measured by barium chromate spectrophotometry, methylene blue colorimetry, and an elemental



**Fig. 1** Schematic diagram of the CSTR system used in the present study

analyzer, respectively. The S-total sulfides was determined by methylene blue spectrophotometric method with original sludge, while S-soluble sulfide was determined by methylene blue spectrophotometric method with liquid produced by filtration of original sludge through 0.45  $\mu\text{m}$  microporous filter membrane (Tian et al. 2020).

#### **H<sub>2</sub>S emission formula based on the sulfide equilibrium**

Equation (1) shows the sulfide ionization equilibrium model and its derivation process (Tian et al. 2020):

$$C_{\text{H}_2\text{S}} = 34S_{\text{T}} / \left( 32 \left( 1 + \frac{K_{\text{S1}}}{10^{-\text{pH}}} + \frac{K_{\text{S1}}K_{\text{S2}}}{10^{-2\text{pH}}} \right) \right) \quad (1)$$

In Eq. (1),  $C_{\text{H}_2\text{S}}$  is the concentration of H<sub>2</sub>S in the liquid phase ( $\text{mg}/\text{m}^3$ ),  $K_{\text{S1}}$  and  $K_{\text{S2}}$  are the second and first equilibrium constants of sulfide, with values of  $7.1 \times 10^{-15}$  and  $1.3 \times 10^{-7}$ , respectively, and  $S_{\text{T}}$  represents soluble sulfide ( $\text{mg}/\text{m}^3$ ) in fermentation broth.

Equation (2) shows the formula for the prediction of H<sub>2</sub>S concentration in the gas phase:

$$C = EC_{\text{H}_2\text{S}} \quad (2)$$

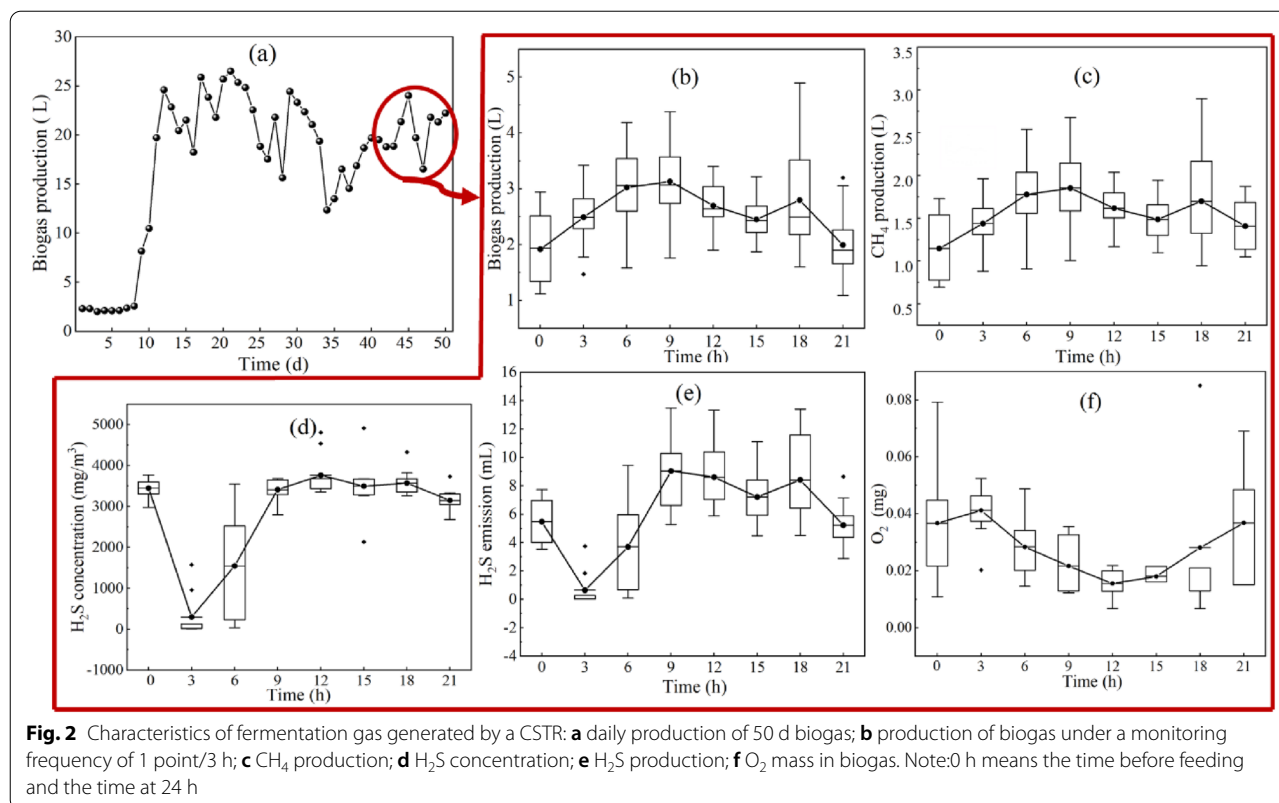
In Eq. (2),  $C$  is the concentration of H<sub>2</sub>S in the gas phase ( $\text{mg}/\text{m}^3$ ) and  $E$  is the Henry coefficient (0.686 kPa at 35 °C).

## **Results and discussion**

### **Characteristics of Biogas, CH<sub>4</sub>, H<sub>2</sub>S and O<sub>2</sub>**

#### **Biogas and CH<sub>4</sub>**

As shown in Fig. 2a, there was an increasing trend in biogas production during AD over 50 days from day 1 to day 10 with a yield of 2.02–10.48 L/d. Biogas production then stabilized from the day 11 to day 50 at a high average yield of  $20.62 \pm 3.43$  L/d. During this stage, the average CH<sub>4</sub> and CO<sub>2</sub> contents of biogas were  $63.21 \pm 0.16\%$  (v/v) and  $36.56 \pm 0.06\%$  (v/v), respectively. Biogas and H<sub>2</sub>S were monitored at 1 point /3 h after 40 days of fermentation. As shown in Fig. 2b, c, biogas and CH<sub>4</sub> showed upward trends during the initial stage of feeding at rates of  $1.92 \pm 0.61$  L/3 h and  $1.15 \pm 0.36$  L/3 h, respectively, at 0 h (before feeding) to  $3.13 \pm 0.13$  L/3 h and  $1.85 \pm 0.45$  L/3 h, respectively, at 9 h (After feeding), after which the gas production rate showed a gradual downward trend. The rates of



biogas and CH<sub>4</sub> production were  $1.99 \pm 0.67$  L/3 h and  $1.41 \pm 0.31$  L/3 h, respectively, by 21 h. The average rates of biogas and CH<sub>4</sub> production were  $2.56 \pm 0.41$  L/3 h and  $1.55 \pm 0.21$  L/3 h, respectively.

### H<sub>2</sub>S and O<sub>2</sub>

As shown in Fig. 6a, the average concentration and release potential of H<sub>2</sub>S were  $3,335 \pm 352$  mg/m<sup>3</sup> and  $1,265 \pm 578$  g/t (TS), respectively, at a monitoring frequency of 1 point/24 h. There were clear differences in the changes in H<sub>2</sub>S concentration under a monitoring frequency of 1 point/3 h to that under a monitoring frequency of 1 point/24 h. As shown in Fig. 2d, the concentration of H<sub>2</sub>S decreased rapidly at the beginning of feeding, from  $3449 \pm 227$  mg/m<sup>3</sup> at 0 h (before feeding) to  $298 \pm 45$  mg/m<sup>3</sup> at 3 h (after feeding), following which it gradually increased and stabilized at 9 h at a concentration of  $3149 \pm 277$  mg/m<sup>3</sup>– $3763 \pm 472$  mg/m<sup>3</sup> from 9 to 21 h. A similar trend was noted in the production of H<sub>2</sub>S (Fig. 2e). The results of the present study were consistent with that of Huang et al. (2014) who showed that the concentration of H<sub>2</sub>S in the methanogenic phase of two-phase AD of food waste first increases and then decreases after feeding, with a maximum H<sub>2</sub>S concentrations of 437 mg/m<sup>3</sup> and 175 mg/m<sup>3</sup> between 8–9 h, and 23–24 h, respectively. The low concentration of H<sub>2</sub>S in

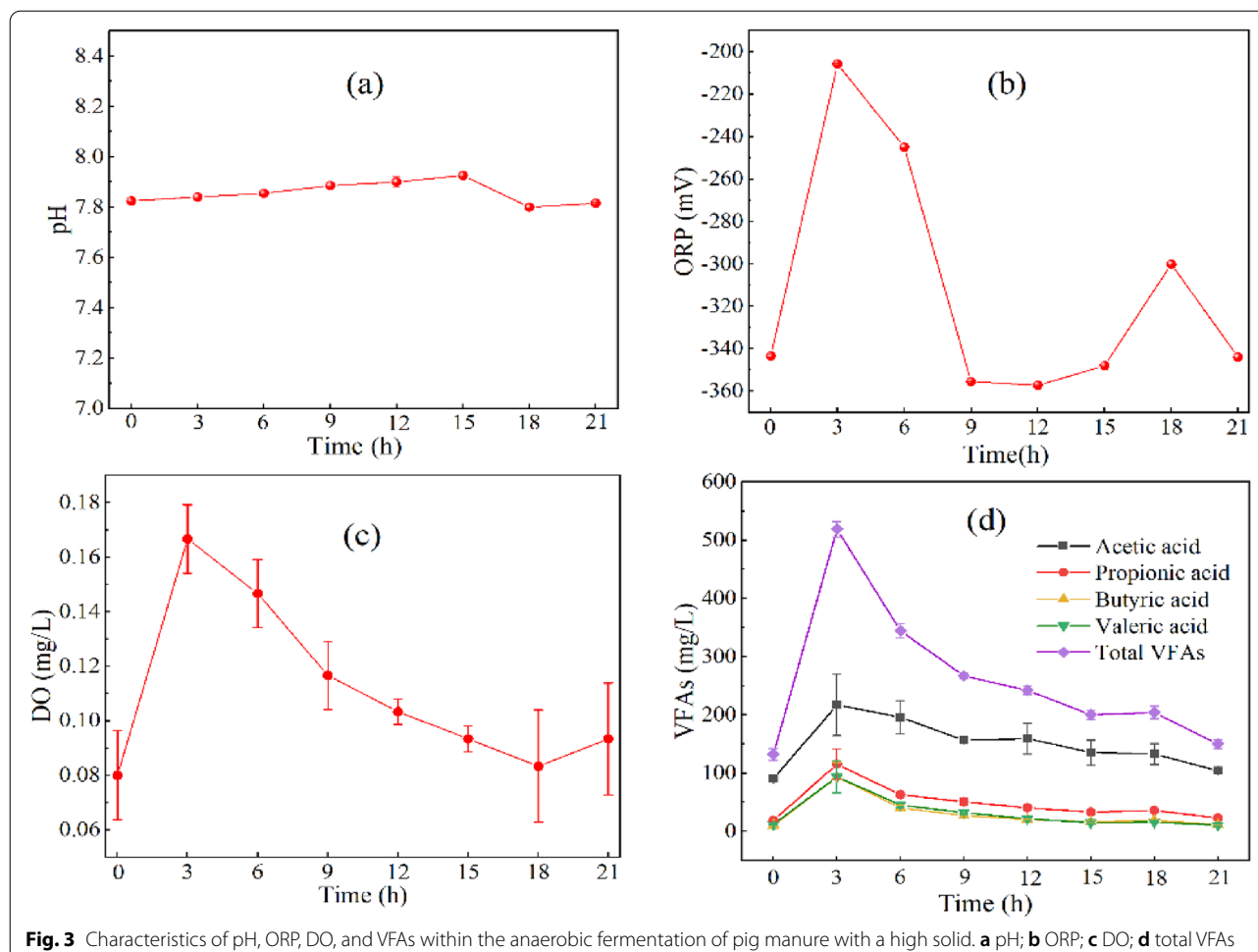
the study by Huang et al. (2014) may be due to the acidified phase in the two-phase anaerobic reactor leading to the early release of a portion of the H<sub>2</sub>S.

As shown in Fig. 2f, O<sub>2</sub> content in biogas components gradually decreased as AD progressed, with a concentration of 1.44% at 3 h, decreasing to 0.99% at 6 h, further decreasing to 0.76% at 9 h, and stabilizing at 0.49–0.69% at 12–21 h. According to these results, the content of O<sub>2</sub> in biogas increased by 15–17 mg, whereas daily atmospheric O<sub>2</sub> carried by the feed was 16–19 mg. Therefore, the increased O<sub>2</sub> in the biogas originated from atmospheric O<sub>2</sub> carried by the feed.

### Characteristics of pH, ORP, DO and VFAs

As shown in Fig. 3a, a stable pH of the CSTR system with high solid pig manure was observed, ranging from 7.80 to 7.93, remaining in a range suitable for the growth of methanogens and indicating a healthy state of fermentation (Chotinath Vongvichiankul 2017). As shown in Fig. 3b, there was a rapid increase in ORP in the reactor within 3 h after feeding, rising from  $-343.4 \pm 0.8$  mV at 0 h to  $-205.8 \pm 0.5$  mV at 3 h. ORP gradually decreased with the progression of AD from  $-244.9 \pm 0.1$  mV at 6 h to  $-355.5 \pm 0.2$  mV at 9 h, following which it stabilized at  $-357.3 \pm 0.2$  mV to  $-300.1 \pm 0.1$  mV. As shown in Fig. 3c, there was a rapid increase in DO in the reactor





**Fig. 3** Characteristics of pH, ORP, DO, and VFAs within the anaerobic fermentation of pig manure with a high solid. **a** pH; **b** ORP; **c** DO; **d** total VFAs

within 3 h after feeding, rising from  $0.08 \pm 0.02$  mg/L at 0 h to  $0.17 \pm 0.01$  mg/L at 3 h. DO tended to stabilize with progression of AD, maintaining a concentration of between  $0.08 \pm 0.02$  mg/L– $0.12 \pm 0.01$  mg/L, indicating a gradual absorption of  $O_2$  by the fermentation broth.

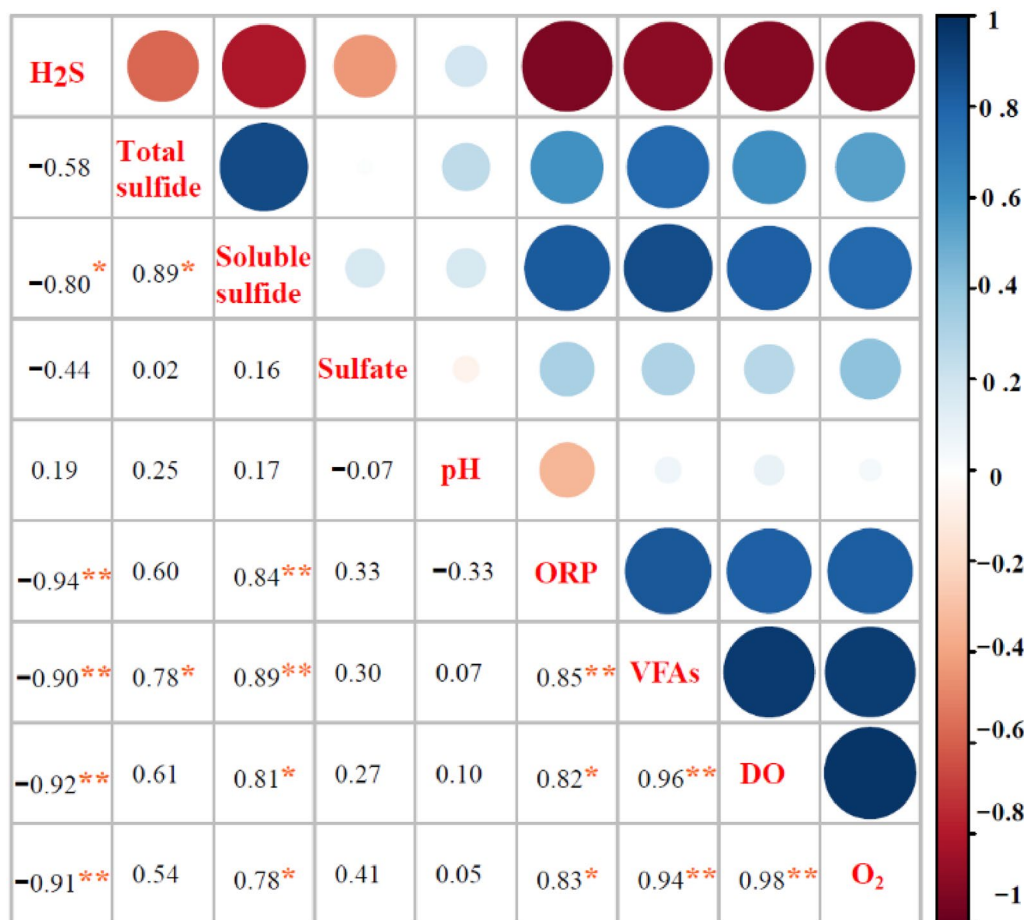
As shown in Fig. 3d, four VFAs, namely, acetic acid, propionic acid, butyric acid, and valeric acid, were produced in large quantities during the initial 3 h of AD. Acetic acid concentration increased from  $90 \pm 1$  mg/L at 0 h to  $217 \pm 52$  mg/L, propionic acid increased from  $19 \pm 1$  mg/L to  $115 \pm 26$  mg/L, butyric acid increased from  $11 \pm 2$  mg/L to  $93 \pm 25$  mg/L, and valeric acid increased from  $12 \pm 1$  mg/L to  $93 \pm 28$  mg/L. Acetic acid was the main component of total VFAs (42% of total VFAs). The concentrations of all VFAs gradually decreased with progression of AD. In a study like to the current study, Andreides et al. (2021) used a solution of ricotta cheese as material for sequential batch AD, with the results of their study showing that VFAs were almost completely consumed after 8 h. Within the present study, the concentration of VFAs of the feed sample at the start

of AD was relatively high at  $2345 \pm 184$  mg/L. On the other hand, a large quantity of dissolved organic matter contained in raw materials can be rapidly transformed into VFAs by microorganisms, resulting in an increase in the initial concentration of VFAs of fermentation (Yin et al. 2021). Since a large number of VFAs were transformed into  $CH_4$  and  $CO_2$  as fermentation progressed, the concentration of VFAs gradually decreased, consistent with the results of previous studies on the AD of pig and chicken manure (Ao et al. 2021; Huang et al. 2016).

There was negligible change in the concentration of  $NH_4^+-N$  in the present study, remaining between 1766 and 2000 mg/L.

#### The relationship between ORP, DO, VFAs and $H_2S$

The present study further examined the correlation between physical and chemical properties of fermentation broth and  $H_2S$  concentration using Pearson correlation analysis. As shown in Fig. 4, the concentration of  $H_2S$  was negatively correlated with  $O_2$  content, ORP, DO and VFAs in biogas ( $P < 0.01$ ), whereas ORP was positively



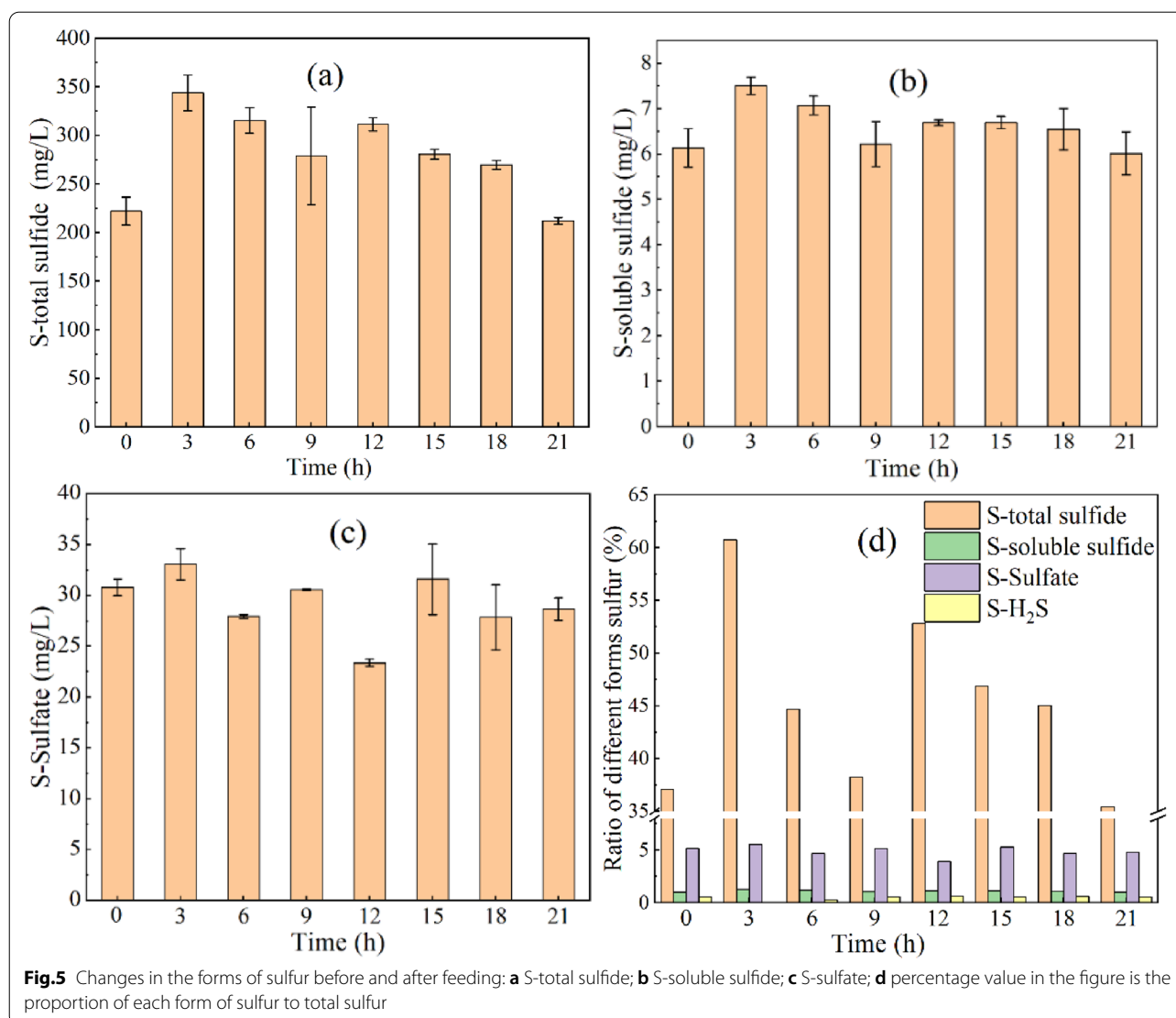
**Fig. 4** Pearson correlation heatmap between physiochemical characteristics and  $H_2S$  concentration. (Note Significance level: \*  $P < 0.05$ , \*\*  $P < 0.01$ ,  $n = 8$ )

correlated with VFAs ( $P < 0.01$ ). The results of the present study showed that an increase in ORP in broth during the fermentation of pig manure from  $-357$  mV to  $-205$  mV resulted in a decrease in  $H_2S$  concentration in biogas from  $3449$  mg/m<sup>3</sup> to  $298$  mg/m<sup>3</sup>. Consistent with the results of the present study, Nghiem et al. (2014) demonstrated a decrease in  $H_2S$  concentration in biogas from  $6,000$  ppm to  $< 30$  ppm with an increase in ORP from  $-320$  mV to  $-270$  mV during AD of sewage. Since the pH of the reactor was maintained within a small range of between  $7.80$  and  $7.93$  in the present study, it can be asserted that pH had no significant influence on  $H_2S$  concentration ( $R = 0.19$ ). Past studies have shown that the initial pH of sludge has an impact on  $H_2S$  generation during AD of abattoir wastewater. For example, Yan et al. (2018) showed that an initial increase in pH of sludge from  $6.5$  to  $8.0$  resulted in an increase in biogas production of  $10.1\%$ , whereas  $H_2S$  concentration decreased by  $44.7\%$ .

#### Variations in different forms of sulfur

As shown in Table 1, there was an average concentration of total sulfur in raw pig manure of  $695 \pm 93$  mg/L, whereas total sulfur in fermentation liquid was  $629 \pm 43$  mg/L, indicating that fermentation did not lead to significant loss in sulfur. As shown in Fig. 5a, S-total sulfide in the reactor increased from  $222 \pm 14$  mg/L at  $0$  h to  $343 \pm 18$  mg/L at  $3$  h, following which it gradually decreased. The concentration of S-total sulfide at  $21$  h was  $212 \pm 3$  mg/L. As shown in Fig. 5d, S-total sulfide accounted for  $36\%$  to  $60\%$  of total sulfur. Therefore, S-total sulfide constituted the main chemical form of sulfur.

As shown in Fig. 5b, there was a rapid increase in S-soluble sulfide in the reactor, from  $6.1 \pm 0.7$  mg/L to  $7.5 \pm 0.2$  mg/L at  $3$  h before fermentation, following which it gradually decreased from  $7.1 \pm 0.2$  mg/L at  $6$  h to  $6.0 \pm 0.5$  mg/L at  $21$  h. As shown in Fig. 5d, S-soluble sulfide accounted for  $0.9$ – $1.3\%$  of total sulfur.



A significant negative correlation was noted between S-soluble sulfide and H<sub>2</sub>S concentration ( $P < 0.05$ ), inconsistent with the sulfide ionization equilibrium model. This result could be attributed to oxidation of H<sub>2</sub>S in the liquid phase during the transfer to the gas phase.

As shown in Fig. 5c, there was a negligible difference in S-sulfate concentration at 0 h at an average concentration of  $29.2 \pm 2.8$  mg/L. Table 1 shows that the S-sulfate concentration of raw material was  $36.4 \pm 0.3$  mg/L, indicating no obvious reduction of sulfate in the fermentation system. The proportion of S-sulfate in total sulfur was 3.9–5.5%, whereas the proportion of H<sub>2</sub>S in total sulfur was 0.0–0.6%.

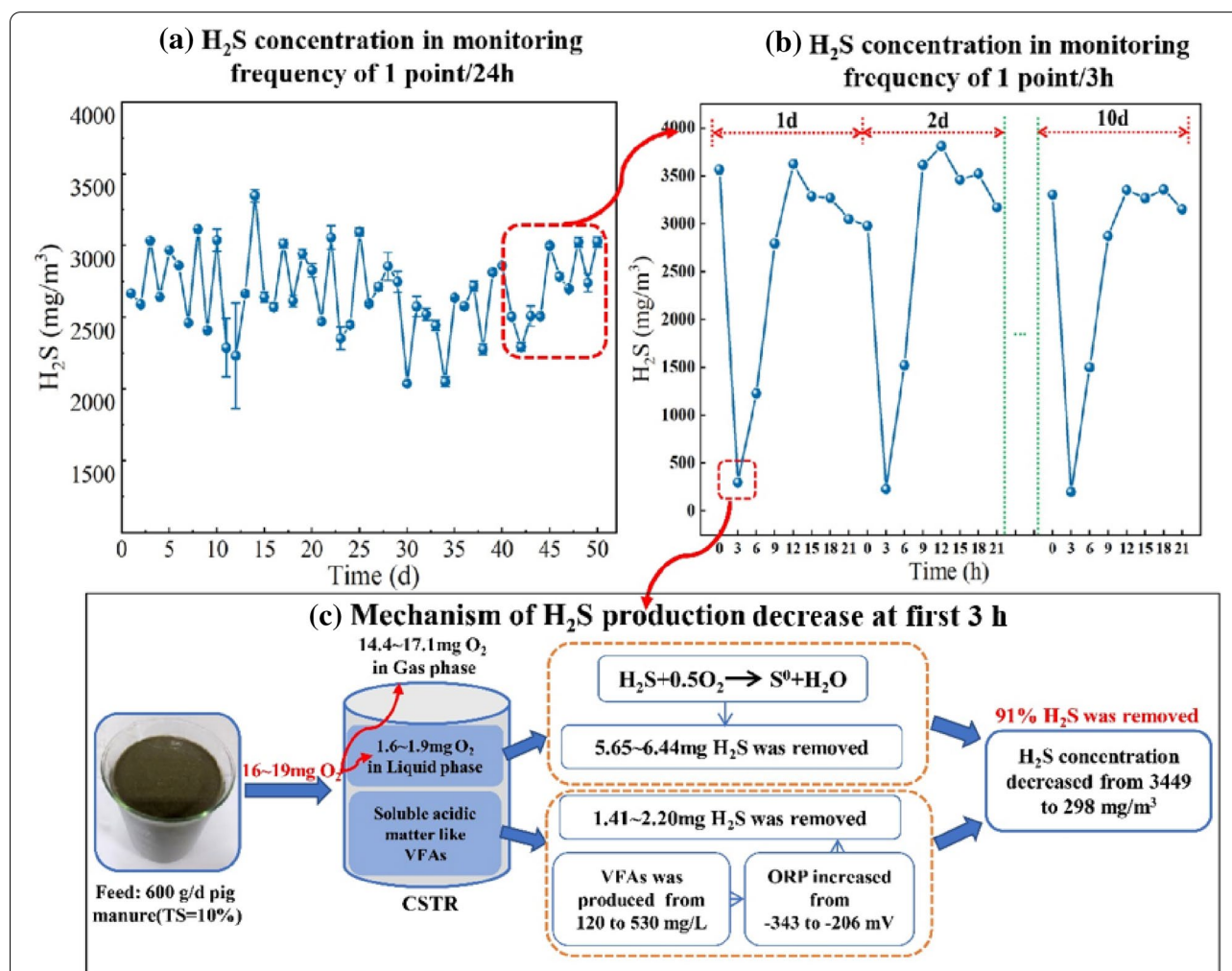
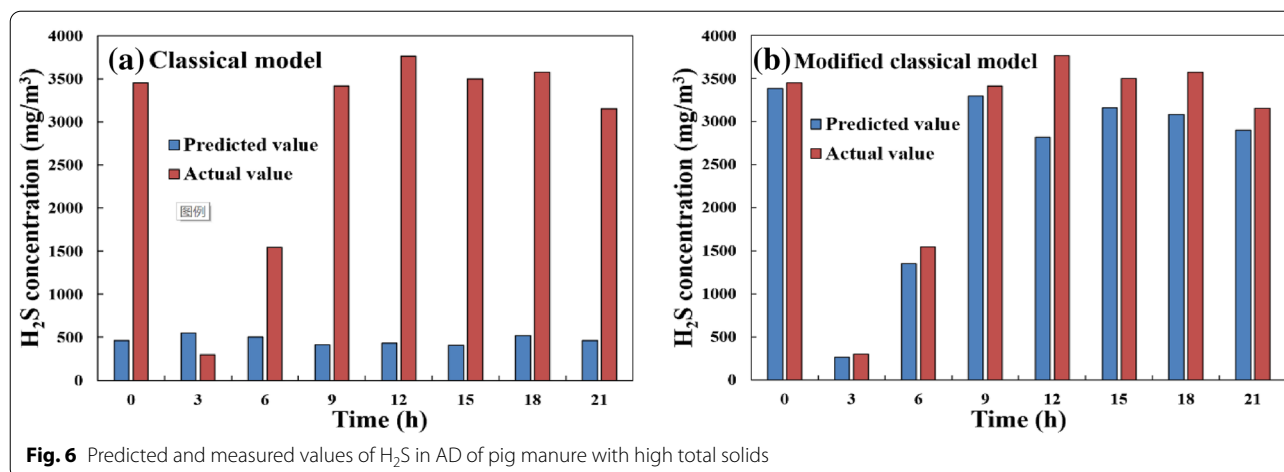
### The mechanism of H<sub>2</sub>S emission

#### Sulfide ionization equilibrium model

The concentration of H<sub>2</sub>S in the fermentation broth was calculated by applying the concentration of soluble sulfide (Fig. 5b) and pH (Fig. 3a) to the sulfide ionization equilibrium model (Eq. 1). Then H<sub>2</sub>S concentration in the gas phase was then calculated according to Henry's coefficient at 35 °C using Eq. 2. As shown in Fig. 6a, besides for at 3 h, the predicted value was only 12–31% of the observed value, indicating an inaccurate prediction.

As shown in Fig. 4, there was very significant negative correlation between the concentration of H<sub>2</sub>S and total VFAs ( $R = -0.9$ ,  $P < 0.01$ ). Therefore, the present study





attempted to modify the sulfide ionization equilibrium model using the concentration of total VFAs. Under a conversion factor of 5.5, the modified model was:  $C = 5.5B_{VFA}EC_{H_2S}$  (note:  $B_{VFA}$  represents the concentration of total VFAs). As shown in Fig. 6b, the accuracy of predictions improved to 72–99%. In summary, the concentration of total VFAs indicated that the correction coefficient of the classical sulfide ionization equilibrium model is 5.5, and application of this coefficient significantly improved the accuracy of the model.

### Mechanism of $H_2S$ release

As shown in Fig. 7a, b, the changes in  $H_2S$  concentration under a monitoring frequency of 1 point/3 h were significantly different from those under a monitoring frequency of 1 point/24 h. This result can be ascribed to the rapid decrease in  $H_2S$  3 h after feeding, which can be attributed to two processes, described below.

The first process is the direct oxidation of  $H_2S$  by  $O_2$ . As shown in Figs. 2f and 4, and the previous analysis, 70–80 mg of air was assimilated by the fermenter during each feed, of which 16–19 mg was  $O_2$ . Approximately 90% of the  $O_2$  was transferred to the gas phase, with the remainder transferred to the fermentation broth (1.6–1.9 mg), with this portion of  $O_2$  available for conversion of  $H_2S$  into zero-valent sulfur (Diaz et al. 2010; Mahdy et al. 2020). This resulted in the removal of 5.49–6.28 mg of  $H_2S$  produced in the first 3 h, accounting for 72% to 82% of the total removal (7.85 mg) (Fig. 7c).

The second process is the increase in ORP resulting from the increase in VFAs and other acidic organic matter during the early stage of fermentation. This led to the oxidation of sulfide. As shown in Fig. 4 and the previous analysis, VFAs had a very significant negative correlation with  $H_2S$  concentration ( $R=0.9$ ,  $P<0.01$ ) and a very significant positive correlation with ORP ( $R=0.85$ ,  $P<0.01$ ). The concentration of VFAs increased rapidly (from  $132\pm10$  mg/L to  $519\pm13$  mg/L) within 3 h of feeding. This result could mainly be attributed to the higher concentration of VFAs in the feed samples of  $2,345\pm184$  mg/L, followed by dissolution of VFAs in the raw materials of fermentation as organic matter was rapidly converted into VFAs during the initial stage. On the other hand, the negligible change in DO concentration in the fermentation broth (Fig. 3c) of between  $0.08\pm0.02$  mg/L and  $0.12\pm0.01$  mg/L was insufficient to affect ORP. Based on the above analysis, the present study proposed that the increase in volatile acids and other acidic organic substances was the main driver of the increase in ORP, which in turn led to the decrease in  $H_2S$ . Like the present study, Nghiem et al. (2014) showed that  $H_2S$  concentration in biogas decreased from 6,000 ppm to 30 ppm as ORP in sludge increased

from  $-320$  mV to  $-270$  mV. In summary, an additional reason for the rapid decline in  $H_2S$  concentration during the first 3 h was the increase in ORP due to the presence of a large quantity of acidic organic matter in the early stage, such as VFAs.

### Conclusions

The present study that variation in  $H_2S$  in a CSTR with high solid pig manure under a monitoring frequency of 1 point /3 h was clearly different from that under a monitoring frequency of 1 point /24 h. Specifically, the concentration of  $H_2S$  rapidly decreased within the first 3 h of fermentation, from  $3449\pm227$  mg/m<sup>3</sup> at 0 h (before feeding) to  $298\pm45$  mg/m<sup>3</sup> at 3 h (after feeding), following which it rapidly increased between 4 and 8 h, and stabilized to between,  $3149\pm277$  mg/m<sup>3</sup> and  $3763\pm472$  mg/m<sup>3</sup> from 9 to 21 h.  $O_2$  contents in biogas, VFAs, and ORP were negatively correlated with  $H_2S$  concentration ( $P<0.01$ ). Mass balance analysis showed that the decrease in  $H_2S$  in the first 3 h could be partly attributed to oxidation of  $H_2S$  by  $O_2$  carried by the feed, and partly to the increase in ORP due to the increase in acidic organic matter, such as VFAs, leading to the oxidation of  $H_2S$ . The accuracy of sulfide ionization equilibrium model was improved by considering the concentration of VFAs. The results of the present study can act as a reference for further research into the regulation of  $H_2S$  in situ in high solid AD by controlling the feed carrying  $O_2$ .

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### Author contributions

CR: investigation, formal analysis, and writing—original draft. He Tengbing: funding acquisition and supervision. CR: investigation. PT: investigation. HC: investigation. TG: investigation. Funding acquisition, writing—original draft, review and editing. All authors read and approved the final manuscript.

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### Availability of data and materials

Not applicable.

### Declarations

### Ethics approval and consent to participate

Not applicable.

### Consent for publication

Not applicable.

**Competing interests**

The authors declare that they have no competing interests.

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