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In-Situ H₂S reduction in biogas fuel for solid oxide fuel cell applications by using cow urine

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ABSTRACT

Biogas, generated from small scale digesters, is a traditional energy source for satisfying the thermal energy demand in off-grid communities. Recent developments in small scale solid oxide fuel cells (SOFCs) technology and progress in research and development of dry reforming, opens perspectives to couple small scale SOFCs with already existing digesters to meet both thermal and electrical energy demand, enabling power access to off-grid communities.

However, one of the major challenges for SOFC integration to small scale digesters is the effect of biogas impurities, such as H₂S, on the performance of SOFCs. Previous work has shown that local operational practices could influence the biogas quality and particularly the H₂S content in the biogas. The here presented research expanded on the use of cow urine instead of water as solvent in manure digestion as a potential operational strategy that enables in-situ reduction of H₂S in the evolving biogas. This research investigated the following hypotheses: 1) urine addition results in a high pH that favours HS⁻ over H₂S, 2) given the presence of metal elements in the cow urine, insoluble metal sulphides are being formed, reducing the biogas H₂S content. The research was carried out by measuring cow urine composition of various samples, assessing the effects of different urine/water/manure mixtures on the evolving biogas-H₂S concentration, and verifying the experimental findings with phreeqc equilibrium speciation. Bio-kinetic modelling, using the anaerobic digestion model nr 1 (ADM1), was subsequently performed to explore the influence of different feed compositions on the H₂S content in the biogas.

It was observed that addition of cow urine in all experiments resulted in an elevated pH of the reactor compared to water dilution, yet both experiments I and II-2 showed an increased maximum H₂S content when urine dilution was applied, compared to water dilution. Cow urine and cow dung characterisation in terms of metals and S, showed that experiment II-1 had the highest Fe:S ratio of 1:0.3–1:0.9. Equilibrium modelling confirmed that despite the positive urine-induced pH effect, the measured Fe:S ratios could indeed be decisive, as with an Fe:S ratio of 1:6 and 1:0.5, the H₂S production at equilibrium was 61 and 10 mL/ kg of solution, respectively. Furthermore, it was predicted through bio-kinetic modelling that inconsistency in feedstock composition may result in temporary H₂S peaks exceeding 400 ppm. Overall, results showed that if a cow urine/manure mixture is characterised by a total metal:S ratio exceeding 1:0.5 and total S content of less than 0.5 mM, then hydrolysed cow urine addition presents an interesting in-situ H₂S cleaning strategy for biogas-SOFC applications.

Nomenclature

AD Anaerobic Digestion

BSP Biochemical gaseous H₂S Potential
SOFC Solid Oxide Fuel Cell

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1. Introduction

Small-scale biogas plants are important to replace the common fossil fuel-based energy sources of off-grid communities, which are growing in number and size and are increasing the energy demand for rural agri-food systems (IRENA and FAO, 2021). The efficient use of renewable energy sources has the potential to decrease fossil-fuel based CO₂ emissions from agro-food systems, which consume 30% of the world's total energy (IRENA and FAO, 2021).

Biogas from anaerobic digestion (AD) usually contains varying fractions of its main compounds CH₄ and CO₂, as well as varying fractions of trace compounds, such as H₂S and volatile organic compounds (VOCs), depending on the source (Rasi, 2009). The produced ratio CH₄:CO₂ in the biogas during AD is determined by the biochemical composition of the organic feedstock and the reactor operational conditions (Van Lier et al., 2020). Therefore, several factors have been reported to influence the composition of biogas from AD, such as the type of fodder for the animals, the source and nature of the waste to be treated, and the design and operational practices of the digester (Godi et al., 2013; Sambo et al., 1995). Biogas from AD of sludge from waste water treatment plants (WWTPs) contains 55 to 65% of CH₄ and 35 to 45% of CO₂ (Rasi, 2009). From organic waste AD, biogas may contain 60 to 70% of CH₄ and 30 to 40% of CO₂, whereas for biogas from landfills, 45 to 55% of CH₄ and 30 to 40% of CO₂ with the rest being N₂ has been reported (Rasi, 2009).

Biogas trace compounds, such as H₂S and volatile organic compounds (VOCs), are also present in varying quantities, depending on the feedstock composition and reactor operation. Biogas trace compounds are commonly referred to as impurities, because of their effects on both human health and energy process equipment. Their effects depend on their concentration in the biogas and the intended application of the biogas. Unlike other trace compounds like siloxanes, which are not common in high concentrations in biogas from small scale manure digesters, H₂S is one of the most common undesired compounds in the fuel for energy process equipment. H₂S also has been identified as one of the factors that contribute to biogas application failure in Africa (Mukumba et al., 2016), while it can also affect the efficiency of the AD process. For instance, high dissolved H₂S concentrations exceeding 0.15 g/L can affect methanogenesis, which can reduce the methane yield (van Leeuwenhoek, 1974; Hulshoff Pol et al., 1998).

Metals have been reported to have a positive effect on the AD process in trace concentrations. The commonly required metals for a proper digestion process include Fe, Cu, Zn, Mn, Ni, Co, Mo, Se, and W (Anwar et al., 2014). If insufficiently present, then a balanced dosage can enhance the methane yield distinctly (Kato et al., 2012; Yaw et al., 2016). Dosing the digester with metals like Fe can also reduce the H₂S content in the biogas (Schmidt et al., 2014), which is due to the formation of metal sulphides. Apart from H₂S content reduction in the biogas, specifically Fe has been reported to enhance methane production and stabilize the AD process, as it was found to be required for cytochromes and ferroxin production in methanogens (Agani et al., 2016; Yaw et al., 2016). In addition, it has been reported that additives, such as FeSO₄, FeCl₃, Ca and Mg-salts and adsorbents, such as charcoal and silica gel, can potentially enhance the rate of biogas production (Yadvika et al., 2004). However, it should be noted that inorganic additives also can become a source of secondary pollution to the environment (Mao et al., 2015). Alternatively, some authors claim that organic additives, such as powdered legumes and leaves of some plants, may enhance the biogas yield by over 18% (Thiruseelvi et al., 2018; Yadvika et al., 2004). In addition to the increased organic load, this also could be due to the presence of trace elements, such as Fe, in green biomass (Guha and Mitchell, n.d.). Additives can also help to maintain favourable conditions in the digester, such as circumneutral pH, a pre-requisite for stabilized biogas production (Yadvika et al., 2004).

A biogas-SOFC energy system is being developed to cost-effectively meet the energy demands of rural off-grid communities in the

developing world. Although, fuel cells costs have been reducing, costs reduction remains a serious challenge (Staffell and Green, 2013). Possibly, overall costs can be further reduced using a trade-off with the biogas quality to be used as the fuel, provided long-term robust operation is not jeopardized. If successful, then a biogas-SOFC system could play an important complementary role in alternative off-grid energy supply systems. However, the presence of H₂S beyond threshold limit is still a challenge for biogas application as reported in Table 1, which is particularly true for biogas-SOFC systems (Aravind and De Jong, 2012). Therefore, cleaning of the gas, regardless of the threshold of the equipment, is mostly preferred (Malone Rubright et al., 2017). Although there are some SOFC materials that have exhibited high tolerance to H₂S, their cost is still a challenge (Saadabadi et al., 2019). On the other hand, it should be noted that cleaning of the biogas also would contribute to both capital and operation & maintenance costs of small-scale biogas-SOFC energy systems (Wasajja et al., 2020).

The use of urine as opposed to water for dilution of digester feed stock is one of the observed operational practices in Uganda. Urine contains cations like Na⁺ and K⁺ that may contribute to stabilize the pH as well as to dose specific metal elements such as Fe, which could act as co-factor in enzymes, enhancing AD efficiency, and precipitate sulphides as FeS (Hindupur, 2018; Zandvoort et al., 2006). In addition to this, urine contains urea (Miah et al., 2017), and when stored, urine is hydrolysed to ammonia and bicarbonate, which increases the pH of urine to >9 (Lindeboom et al., 2018; Udert et al., 2003). Both trace metals and high pH can influence the AD process and hence biogas composition, including the H₂S content. Therefore, this research was aimed at investigating the effect of cow urine addition instead of water on H₂S concentration in the biogas. To the authors knowledge, so far, no studies have been conducted to investigate the feasibility of urine as a bio digester additive to enhance the AD process, as well as a possible in-situ H₂S cleaning method.

2. Materials and methods

The study was carried out in five steps, which included: 1) characterisation of urine, 2) adaptation of the standardised biochemical methane potential (BMP) test towards a standardised biochemical gaseous H₂S potential (BSP) test using Dutch cow manure, 3) set-up and execution of two experimental BSP tests under field conditions of rural Uganda, 4) geochemical speciation modelling and 5) bio-kinetic modelling of H₂S production combined with geochemical speciation following the approach of Flores-Alsina et al. (Flores-Alsina et al., 2016). The BSP test is similar to the standardised BMP test (Holliger et al., 2016), with the difference that the BSP test is focused on gaseous H₂S production potential as opposed to methane generation potential.

2.1. Characterisation of urine

Fresh cow manure samples were collected from a farm in Delft (Hoeve Biesland), the Netherlands. Cow urine was collected from a farm in Enschede, the Netherlands. Samples were stored at 4 °C. 1.5 mg of urine and cow dung samples were diluted to 50 ml with demineralised water and HNO₃ and used for further analysis to determine the elemental and S concentration. Sulphur and other elemental composition analysis of cow dung and urine samples were carried out by using ICP-OES 1285300DV (Perkin Elmer Optima, Waltham, Massachusetts, USA) following the same procedure as described in Wasajja et al. (Wasajja et al., 2021).

2.2. Experimental procedure for the measurement of gaseous H₂S in cow urine & manure digestion

2.2.1. Experiment I: BSP in laboratory environment

The BSP test was carried using an automated methane potential test system (AMPTS, Bioprocess Control, Sweden) with 15 cells (Keuckens

Table 1
Biogas impurity thresholds depending on the biogas application.

Gas application	Upgrading requirement	H ₂ S threshold	Siloxanes Threshold	Other VOCs threshold	Reference
Kitchen stove	Heating value comparable to natural gas	< 10 ppm	n.a.	n.a	(Sun et al., 2015)
Gas boiler	Upgrading may not be required.	< 250 ppm			(Sun et al., 2015)
CHP engines	> CH ₄ : 35% mol	545–1742 ppm*	9–44 ppm*	60–491(Cl) ppm*	(Sun et al., 2015)(Arnold, 2009)
Stirling engine	> CH ₄ : 35% mol	2800 ppm*	0.44 ppm*	232 ppm**	(Arnold, 2009)
Natural gas grid injection	> CH ₄ : 95% vol CH ₄ : 70–98% mol	< 5 mg/m ³ 2–15 mg/m ³	n.a.	< 120 ppm**	(Hagen and Polman, 2001)(Lanzini et al., 2017)
Vehicle fuel	> 96% mol	5 mg/m ³	n.a	n.a.	(Sun et al., 2015)
Gas turbines	Upgrading may not be required	<10,000 ppm*	< 0.087 ppm*	< 1500 ppm**	(Sun et al., 2015)(Arnold, 2009)
Micro turbines	Upgrading may not be required	25–70,000 ppm*	< 0.01 ppm*	200 ppm**	(Arnold, 2009)
High temperature Fuel cells	Up grading may not be required due to possibilities of dry reforming (Assabumrungrat et al., 2006)	< 1 ppm*	< 0.01 ppm*	< 5 ppm**	(Arnold, 2009)

n.a. = not available

* halogens in biogas.

* mg/m³ of CH₄.

** mg/m³ of Sulphur.

et al., 2018). The test was performed in triplicate. In the setup, glass serum bottles with a working volume of 400 ml and head space of 100 ml were used. The temperature of the bottles was maintained by a thermostatic water bath at 25 °C for 40 days. The serum bottles were stirred at 120 rpm for 180 s after every 30 s of non-stirred conditions. Bottles were filled with 300 g of cow dung after applying a dilution in the ratio of 1:1. Each bottle was flushed with N₂. To achieve homogeneity, the inoculum was mixed by using a blender. K₂SO₄ solution was used to change the S/COD ratio. 0.5 ml of a 1 M K₂SO₄ solution was added to the cells 1–3, and 4–6, while the cells 7–9, 10–12 and 13–15 contained cow dung diluted with 50% urine and 50% water, cow dung diluted with urine, and cow dung diluted with water only, respectively (Table 2). Cow manure functioned both as substrate and inoculum, to enable comparison to the field tests conducted in Uganda.

The next step was to adjust the BMP procedure to enable the prediction of the BSP. In the AMPTS, a water lock containing 3 M NaOH solution is included, that is used to directly capture CO₂ from the biogas and enable the subsequent measurement of CH₄ only. Given the pK_a of 7.2 of the H₂S/HS[−] equilibrium (Perrin, 1982), all produced H₂S is captured as well by the NaOH solution. Therefore, it is possible to use the same setup to analyse the BSP potential by analysing the total S concentration in the NaOH solution by ICP-OES, assuming that the redox state remains anaerobic until the end of the experiment. The metal element concentration in cow dung and urine that were used in the AMPTS experiments was also analysed using the ICP-OES, following the same sample destruction procedure as described by Wasajja et al. (Wasajja et al., 2021a). The captured sulphur in NaOH solution was used to calculate the H₂S produced per kg of manure.

2.2.2. Experiment II: Field-based BSP

The two field-based experiments II-1 and II-2 were carried out to further investigate the effects of urine on H₂S formation from cow dung. Fresh urine was collected from a Ugandan farm. It was left to hydrolyse

for 30 days under atmospheric conditions. Fresh cow dung was also collected on the day of the start of each experiment from the same farm. Water was collected from a tap supplied by pumped water from an underground borehole.

In both the field-based experiments II-1 and II-2, nine 10 l reactors were constructed out of plastic spray bottles (Appendix 1). They were equipped with a manometer pressure gauge (Festo, Germany) with a range of 0–1 bar to monitor the biogas pressure. The H₂S gas was sampled through the outlet of the bottle using a hand sampling pump (Dräger accuri, Luebeck, Germany). The H₂S content in the biogas was measured during sampling using the same hand sampling pump equipped with H₂S measurement tubes (Dräger, Luebeck, Germany) with ranges of 0–2000 ppm and 0–7% (v/v).

In both experiment II-1 and II-2, reactors 1–3 were fed with 2 kg of cow dung diluted with 2 l of water, reactors 4–6 with 2 kg of cow dung diluted with 2 l of hydrolysed urine and reactors 7–9 with 2 kg of cow dung diluted with 1 l of hydrolysed urine and 1 l of water. It is highly important for the interpretation of the results to note that both experiments were conducted at a different time point with different cow dung and urine composition, albeit manure samples were collected from the same farm.

The second difference was that in experiment II-1, biogas pressure was left to accumulate, while biogas samples were taken. Consequently, in subsequent mass balance calculations, pre- and post-sampling pressure had to be corrected for. However, in experiment II-2, biogas pressure was left to accumulate until sampling, after which all accumulated gas was released to equilibrate to atmospheric pressure. Then biogas pressure was again allowed to accumulate until the next sampling point. This cycle was repeated until pressure no longer accumulated.

2.3. Theoretical geochemical Sulphur speciation in cow urine/manure digestion at equilibrium conditions

The aim of geochemical speciation modelling was to calculate and quantitatively determine the influence of urine mineral composition and total input sulphur on the theoretical gaseous H₂S equilibrium content. Based on the urine and manure composition and differences in salinity in each of the three experiments, Phreeqc software was used, for its inclusion of the Pitzer based ion activity calculations (Pitzer, 1973), to model sulphur speciation at equilibrium under the prevailing conditions in the gas, liquid, and solid phase (“Phreeqc,” 2019). As input parameters, the calculated total mass concentrations in cow manure and urine based on ICP-OES analysis were used (Table 3). As output, the

Table 2
Inoculum composition in AMPTS cells.

Cell No.	Inoculum
1–3	Cowdung + water +0.5 ml of 1 M K ₂ SO ₄
4–6	Cowdung + urine +0.5 ml of 1 M K ₂ SO ₄
7–9	Cowdung +50% urine +50% water
10–12	Cowdung + urine
13–15	Cowdung + water

Table 3

Element concentration in urine and cow dung used in experiments I, II-1 and II-2.*

Exp	Solvent	Substrate	Trace metals (mM)				Macro cations (mM)				Macro anions (mM)		Sum (meq/L)	Sum (meq/L)
			Fe	Mn	Pb	Zn	Na	K	Ca	Mg	TP	TS		
I	Urine		0.0	0.0	0.0	0.0	0.1	1.4	0.2	0.1	0.1	0.1	10.0	0.4
	Urine		0.1	0.0	0.0	0.0	0.1	1.4	0.2	0.1	0.1	0.1	9.8	0.4
	Urine		0.1	0.0	0.0	0.0	0.1	1.4	0.2	0.1	0.1	0.1	9.7	0.4
	Water	Cow manure	0.1	0.0	0.0	0.0	0.1	1.2	1.6	0.6	0.9	0.4	9.6	3.6
	Water	Cow manure	0.1	0.0	0.0	0.0	0.1	0.8	1.5	0.7	0.9	0.4	8.2	3.7
	Water	Cow manure	0.1	0.0	0.0	0.0	0.1	1.7	1.6	0.6	0.9	0.5	13.3	3.8
II-1	Water	Cow manure	0.9	0.1	0.0	0.0	0.1	0.8	1.8	0.5	0.5	0.3	11.0	2.1
	Water	Cow manure	0.8	0.1	0.0	0.0	0.1	0.6	2.0	0.5	0.6	0.3	10.3	2.2
	Urine		0.0	0.0	0.0	0.0	0.0	5.9	0.0	0.1	0.0	0.2	8.4	0.3
	Urine		0.1	0.0	0.0	0.0	0.0	5.7	0.1	0.2	0.1	0.2	8.1	0.5
	Urine	Cow manure	0.6	0.1	0.0	0.0	0.2	2.9	1.0	0.5	0.3	0.2	15.0	1.4
	Urine	Cow manure	0.9	0.1	0.0	0.0	0.2	3.5	2.4	0.7	0.6	0.4	20.7	2.6
	Water	Cow manure	0.4	0.1	0.0	0.0	0.1	0.6	1.0	0.4	0.3	0.1	10.4	1.0
	Water	Cow manure	1.0	0.1	0.0	0.0	0.2	0.9	1.7	0.5	0.4	0.3	14.9	1.8
II-2	Urine		0.0	0.0	0.0	0.0	0.0	7.1	0.0	0.2	0.0	0.2	9.2	0.4
	Urine		0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.2	0.0	0.2	9.0	0.4
		Cow manure	0.4	0.1	0.0	0.0	0.1	1.1	3.5	0.6	0.9	0.4	14.0	3.5
	Water	Cow manure	0.0	0.0	0.0	0.0	0.1	0.5	0.1	0.1	0.0	0.0	4.9	0.1
	Water	Cow manure	0.3	0.0	0.0	0.0	0.0	0.6	1.2	0.3	0.3	0.1	5.9	1.3
	Water	Cow manure	0.3	0.0	0.0	0.0	0.0	0.6	1.2	0.3	0.3	0.1	6.0	1.3
	Urine	Cow manure	0.5	0.1	0.0	0.0	0.1	3.8	2.5	0.7	0.7	0.4	14.5	3.0
	Urine	Cow manure	0.5	0.1	0.0	0.0	0.1	3.7	2.3	0.7	0.7	0.4	13.7	3.0

* Concentration in 1.5 mg of sample diluted to 50 ml demineralised water and HNO₃.

equilibrium metal concentrations, pH, and H₂S content in the biogas were calculated and compared with the measured gaseous H₂S content in the three experiments. The applied 4 scenarios were: 1. Using water as a solvent, considering element concentrations of cow dung only; 2. Using urine as a solvent, considering element concentrations of both cow dung and urine; 3. Effect of increasing SO₄²⁻ concentration in the influent, considering high sulphate content in the feedstock; and 4. Effect of increasing Fe concentration in the influent, considering high Fe content in the feedstock. For the calculations, it was assumed that under anaerobic conditions all sulphate would be converted to H₂S/HS⁻ by sulphate reducing bacteria (SRB). Details of the used codes are presented in appendix 2.

2.4. Prediction of dynamics in gaseous H₂S biogas content in continuous cow urine/manure digestion

The bio-kinetic anaerobic digestion model nr. 1 (ADM1) was used to simulate the effects of using urine instead of water as a solvent during AD of cow manure to predict biogas and H₂S production over time. The model was adapted from Flores-Alsina et al. (Flores-Alsina et al., 2016) and contained a metal speciation module, similar to the phreeqC approach as introduced in section 2.4. The model was adapted to the calibrated parameters for cow manure digestion as reported by Wichern et al. (Wichern et al., 2008) in appendix 3, concerning the parameters: disintegration constant (k_{Dis}), acetate uptake rate ($k_{m,ac}$), upper pH limit for acidogens ($pH_{UL,acid}$), lower pH limit for acidogens ($pH_{LL,acid}$), propionate uptake rate ($k_{m,pro}$), half saturation coefficient for propionate uptake ($K_{S,pro}$), half saturation coefficient for hydrogen uptake (K_{S,H_2}) and nitrogen content of composite and inert material ($N_{xc,i}$). The influent parameters were adjusted as shown in appendix 4. Four scenarios were modelled, which included: i) cow dung with water as solvent, ii) cow dung with urine as solvent, iii) cow dung with diluted urine as solvent, iv) increased sulphur concentration in cow dung with diluted urine as solvent. For the urine scenarios, inorganic nitrogen concentration was increased from 2.31×10^{-3} to 7.68×10^{-3} – 10.02×10^{-3} mg/l. Since urine contains sulphur as sulphate (Miah et al., 2017), the sulphate concentration was doubled for concentrated urine and increased by 1.5

times for diluted urine. In addition, the concentrations of trace elements of urine + cow manure were used according to results of elemental analysis (Table 3).

3. Results

3.1. Cow urine and manure composition

The composition of cow urine and cow manure used in experiments I, II-1 and II-2 regarding sulphur and the different elements is shown in Table 3, which gives an overview of the molar elemental composition measured by the ICP-OES. The raw elemental data has been converted into mM and has been clustered into trace metals, which, based on their literature reported K_{sp} values, are prone to form precipitates with sulphide. The sum of the macro cations Na⁺, K⁺, Ca²⁺, and Mg²⁺ as well as the macro-anions PO₄³⁻ (TP) and S²⁻ (TS) is reported in meq/L, to facilitate evaluating their potential role in reactor alkalinity and potential influence on reactor pH. Even without NH₄⁺ having been measured, the urine adds a significant cationic concentration to the substrate mixture.

3.2. Gaseous H₂S production in cow urine and manure digestion

3.2.1. Experimental results

Table 4 presents the total biogas production and the calculated total amount of H₂S produced, as well as the assessed Fe:S ratio, total S in the feed and pH in experiment I, experiment II-1 and II-2. Results showed that urine as solvent affected the H₂S content in the biogas both positively and negatively.

Through the positive controls, bottles 1–6, it was indicated that the method of capturing the H₂S, in the 3 M NaOH solutions gave a reasonable accuracy in recovering the spiked 0.5 M K₂SO₄. Unfortunately, the general performance of biogas production could not be considered as a sound positive control, likely because no adapted inoculum was added, the lag phase exceeded the experimental time of 30 days. Therefore, further analysis has been limited to a general comparison between H₂S produced in either the urine or water diluted Dutch

Table 4Total biogas and total H₂S production and relevant parameters influencing the H₂S content in biogas in the BSP experiments.*

Biogas and H ₂ S production; parameters influencing biogas H ₂ S content	Solvent	Experiment I	Experiment II-1	Experiment II-2	Description
Total Biogas Production (L/kg of manure)	H ₂ O	0.88 ± 0.10	8.8 ± 4.7	92.5 ± 4.8	H ₂ S content in biogas depends on absolute production of both H ₂ S and CH ₄ /CO ₂
	Urine	0.74 ± 0.07	9.4 ± 7.7	76.8 ± 9.6	
Total H ₂ S Production (mL/kg of manure))	H ₂ O	41.1 ± 0.1	4.4 ± 0.1	18.1 ± 4.6	
	Urine	51.1 ± 0.2	3.1 ± 1.8	40.9 ± 7.3	
Total molar S (mM)**	H ₂ O	0.4	0.3	0.4	Increased urea and ammonium, will have a pH increasing effect resulting in increased HS ⁻ speciation
	Urine	0.5	0.5	0.6	
pH	H ₂ O	6.0–6.1	7.1–7.2	6.5–6.6	
	Urine	7.0–7.6	8.3–8.4	8.4–8.5	
Fe:S (molar ratio)	H ₂ O	1:4–1:9	1:0.3–1:0.9	1:0.6–1:1.8	Increased metal content will decrease concentrations HS ⁻ and H ₂ S through metal-sulphide precipitation
	Urine	1:2.5–1:6.3	1:0.5–1:0.7	1:1.5–1:2.0	

* The biogas and H₂S production from all the experiments I, II-1 and II-2 is presented in appendix 1.

** in 50 ml diluted samples.

cow manure. Results obtained from laboratory BSP experiments (experiment I) showed that the addition of urine, despite the increase in alkalinity, resulted in an increased H₂S-production of 51 mL/kg cow manure compared to 41 mL/kg cow manure for the water diluted bottles. In experiment II-1 less H₂S was produced in the urine diluted triplicate experiment, but also in this experiment, the biogas production was below expectation, likely because of the visually observed gas leakages. The latter experiment produced biogas between ~6.5 and 9.0 L/kg of manure, but showed a higher H₂S content when urine was utilized. It is noteworthy from the experimental results that urine also affects the biogas production quantity; results of Experiment II-2 showed a pronounced negative effect (Table 4).

If only the pH increase, induced by the increased alkalinity of the urine, was of importance, all the three urine diluted experiments should have produced less gaseous H₂S compared to their water counterparts. However, this was not observed. As such, also the total S concentration and Fe:S ratio are presented in Table 4. Due to the low concentrations of all other trace metals and iron being the most dominant one, the Fe:S

ratio was determined and not the sum of all trace metals. It was anticipated that in case of a high Fe:S ratio, i.e., excess iron, the BSP would decrease and with a lower Fe:S ratio, the BSP should increase compared to experiments in the same pH range.

Results from experiment I showed that despite the relatively low pH and an unfavourable Fe:S ratio, the H₂S production per kg of manure is still very low. This low production is likely due to the low concentration of both iron and sulphur and the low stripping effect, since there was only very little biogas produced. For experiment II-1, the favourable Fe:S ratio, seems to be reflected in a low BSP. Experiment II-2 on the other hand, shows a relatively high H₂S production, despite the favourable Fe:S ratio and the high pH. Nevertheless, because of the tenfold higher biogas production, the resulting H₂S concentration is still very low in experiment II-2.

3.2.2. Chemical speciation of Sulphur in cow urine & manure digestion

To acquire more in-depth insight in the multiple parameter interaction on the speciation of S, the measured results were compared with

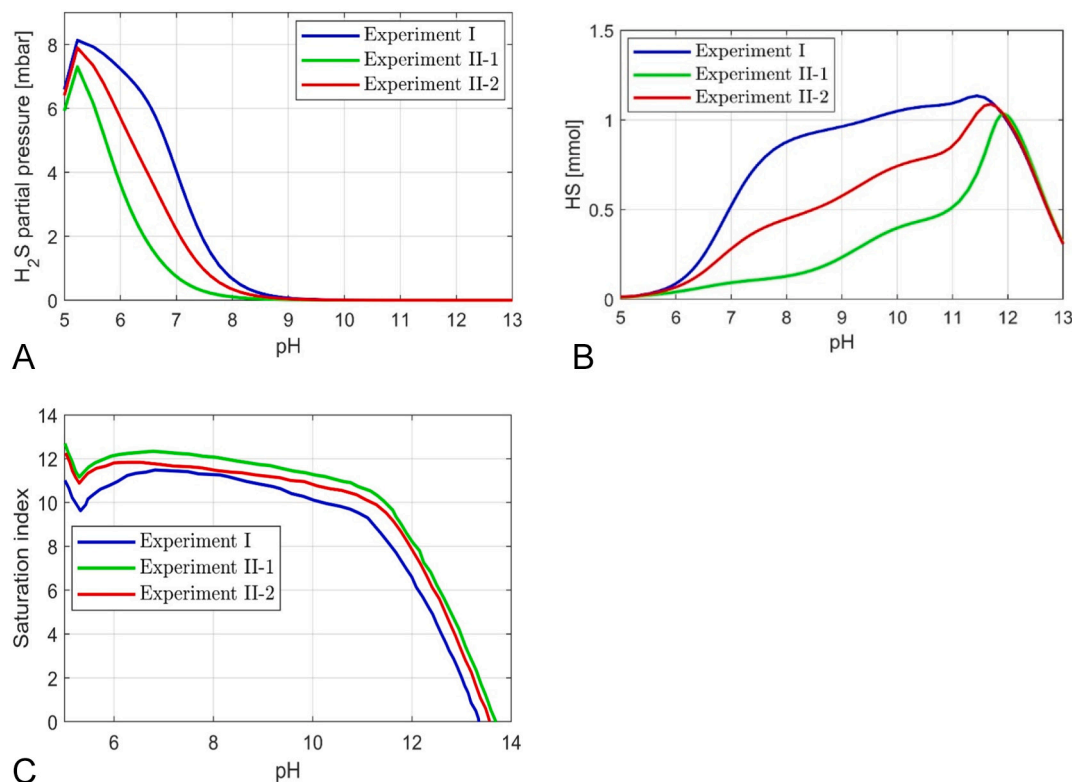


Fig. 1. Effects of pH and Fe on S speciation in Experiment I, II-1 and II-2 with 100% urine dilution. 1 A shows the effect of pH on H₂S partial pressure in the biogas, 1B shows the effect of pH on the HS⁻ concentration in the liquid phase, and 1C depicts the Fe–S saturation index in all experiments.

the outcomes of equilibrium modelling using PhreeqC for the 3 urine dilution experiments. The assessed liquid matrix concentrations (Table 3) and pH (Table 4) were used as input parameters. The results are plotted in Fig. 1A to 1D and the relevant experimental pH range is indicated with dotted lines.

PhreeqC results showed that pH had a great effect on the H_2S partial pressure in the biogas (Fig. 1a) and that an increase in pH exceeding 7.0 sharply reduced the H_2S partial pressure. Results clearly showed that differences in influent composition affected the pH and the resulting H_2S partial pressure in the biogas. Modelling results agreed with the BSP experiments, in which reactors with urine showed a different resulting H_2S content and pH. Experiment II-1 with highest Fe:S had the highest proportion of HS^- as compared to experiment I and II-2 with lower Fe:S ratios. It should be kept in mind that also the cation species Na^+ , K^+ , Ca^{2+} , Mg^{2+} contribute to S speciation (Table 3). From Fig. 1C, it can be seen that the liquid is highly saturated with respect to FeS_2 (pyrite) and this indicates that in all three experiments, any available iron will precipitate S in the stoichiometric ratio of the precipitate. It is noteworthy that also the saturation index of mackinawite, having a 1:1 M Fe:S ratio, indicated super saturation (data not shown). In addition, also other trace metals appeared supersaturated for S precipitate formation, such as, MnS, PbS and ZnS (data not shown).

Modelling experiment I, II-1 and II-2, considering the same Fe:S ratios as measured in the experiments diluted with urine, showed that an increase in Fe:S ratio resulted in a decrease in the H_2S content in the gas phase. Using the scenario of experiment I, with an Fe:S ratio of 1:6, the resulting H_2S production was 90 mL/kg of feedstock at a pH of 7.0 (data not presented here). For experiment II-1 and II-2, with an Fe:S ratio of 1:05 and 1:1.8, the H_2S production was 16.7 mL/kg of feedstock and 49.5 mL/kg of feed stock, respectively. Apparently, by decreasing the Fe:S ratio from 1:0.5 to 1:1.8, the increase in H_2S production is more than doubled. Therefore, doubling the S concentration in the substrate can potentially double the H_2S concentration in the biogas if pH remains constant.

The PhreeqC speciation model, with urine and manure composition as input parameters, also confirmed that CO_2 speciation followed, according to expectations, the same trend as H_2S under these conditions. The higher the pH, the lower the CO_2 content in the gas. Therefore, for technologies that aim at biogas cleaning and upgrading, CO_2 and H_2S removal compete for cation availability. Overall, a higher pH than circumneutral would be preferred from the perspective of gas composition, though too high pH (typically >8.5) may hinder the biological process (Sambo et al., 1995). Also, the free NH_3 content in the liquid and biogas is expected to be higher at a high pH, potentially reaching inhibitory levels for the methanogenic biomass.

3.3. Prediction of dynamics in the biogas gaseous H_2S content during continuous cow urine/ manure digestion

Under field conditions, rural digesters are often intermittently fed. The biokinetic model ADM1 was used to simulate the biogas H_2S content of a continuous flow reactor, while incorporating a chemical S speciation model, similar to the phreeqC model, following the approach and code developed by Flores-Alsina et al. (Flores-Alsina et al., 2016). Fig. 2 shows the ADM1 results for the biogas H_2S concentration using water, urine, and diluted urine as the solvent. The parameters for the model input are shown in appendix 2 and they were based on literature data (Miah et al., 2017) and the metal element analysis presented in Table 3. The flow rate of the digester was left at the default value of 188 m³/d and the temperature was set to 25 °C mimicking the average ambient temperature in Uganda. A final H_2S content of 280 ppm in the biogas was obtained for water as the solvent and a digester pH of 7.0. For urine as the solvent the H_2S content was 130 ppm at a pH of 7.4, despite the doubling of the total S concentration. Comparing the experiments with diluted urine (1:1) and diluted urine with increased SO_4^{2-} concentrations, results showed that an increased SO_4^{2-} content resulted in an

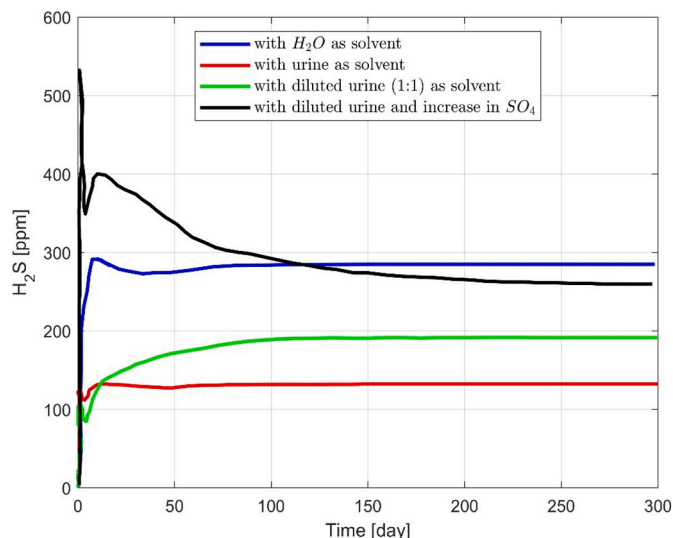


Fig. 2. Dynamic profile of H_2S content in the biogas with the use of different solvents, H_2S concentration with H_2O as solvent, H_2S concentration with urine as solvent, H_2S concentration with diluted urine (1:1) as solvent and H_2S concentration for diluted urine with increased SO_4 concentration from 1.49×10^{-4} mg S/L to 4.7×10^{-4} mg/L.

*The limit for SOFC is less than 1 ppm.

increased biogas H_2S concentration (Fig. 2). The increased biogas H_2S concentration applying diluted urine as solvent indicated that if urine is to be used as an in-situ H_2S reduction mechanism, care should be taken to determine its sulphur concentration in advance. Urine with high SO_4^{2-} concentrations may require a higher degree of dilution to keep the digester sulphur loads to an appropriate level. It must be noted that more dilution also would concomitantly reduce the ammonia concentration, resulting in a lower pH.

Common operational practices of small-scale biogas digesters result in varying feed quantities, depending on the availability of feedstock (Wasajja et al., 2021). Also, there is no standard feeding timetable (Wasajja et al., 2021). This non-continuous feeding scenario and inconsistency in feedstock composition, based on results presented in this chapter, will most likely lead to a variable biogas H_2S content in ranges that could be detrimental to SOFC operation.

4. Discussion

4.1. Comparison of experimental and theoretical biogas H_2S concentrations using cow urine/water as dilution of cow manure

Previous work (Wasajja et al., 2021) had shown that Ugandan manure digesters are characterised by large fluctuations in the biogas H_2S content which appeared related to the addition of cow urine as solvent. Results obtained from experiments in our current work showed that using urine as the solvent indeed affected the H_2S content in the biogas, albeit both positively and negatively. It was hypothesized that the difference in H_2S content would be attributable to the urine and cow dung mixture composition and more specifically to the Fe:S ratio, the pH, and the total sulphur content of the feed stock. To verify this hypothesis, the experimentally determined composition of cow dung diluted with 100% urine was used to calculate the sulphur speciation and a comparison was made between the calculated and measured soluble iron and total sulphur concentration, as well as the produced gaseous H_2S (Fig. 3).

Evaluating both the measured and modelled results indicated that at an Fe:S ratio of 1:6.1 and pH 7.3 (Experiment I), the model can predict a relative rapid rise in H_2S to 50–60 mL/kg of cow manure. A high Fe:S ratio combined with a high pH (8.4), both experimentally assessed as

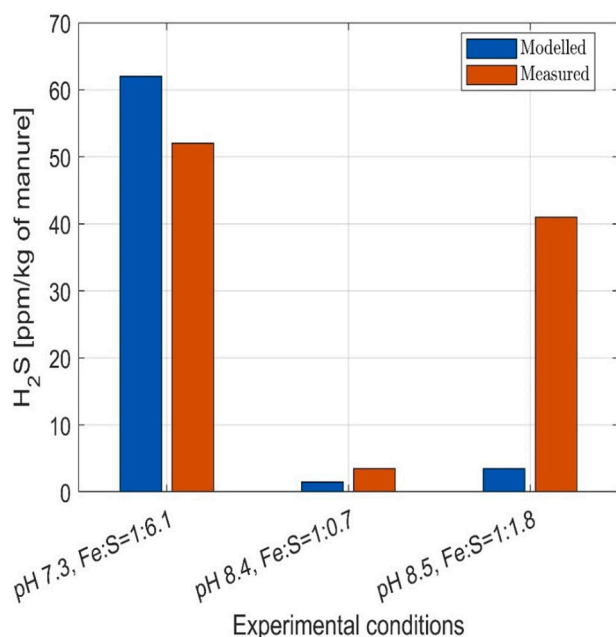


Fig. 3. Comparison of the total amount of produced gaseous H_2S between experimental and modelled values using 100% urine dilution.

well as in the model, resulted in an accurate and low production of gaseous H_2S (Experiment II-1). Experiment II-2 is characterised by a low model prediction of 3.2 mL/kg of cow dung, but a high actual measured value of 40 mL/kg of cow dung.

Results listed in Table 4 showed that experiment I, experiment II-1, and II-2 had different Fe:S ratios, which were also dependent on the used solvent (urine or water). The average Fe:S ratio for reactors diluted with urine from experiment I, experiment II-1, and experiment II-2 was 1:6.1, 1:0.7, 1:1.8, respectively. Modelling with PhreeqC using the measured Fe:S ratios with reactors diluted with 100% urine from all experiments clearly showed that the prevailing Fe:S ratio influenced the resultant H_2S in the gas, which clearly was also pH dependent. Our results corroborate with Schmidt et al. [14], who reported that metal elements are reported to not only enhance the anaerobic digestion process but also to reduce the H_2S content in the gas phase, since they react with HS^- / S^{2-} to form metal sulphides which remain in the liquid phase (Schmidt et al., 2014). The Fe:S ratio-depending on modelled resultant H_2S production agreed well with the measured results (Fig. 3). PhreeqC model results showed that the lower the Fe:S ratio in the feedstock diluted with urine, the higher the resultant H_2S in the gas. Experiment I, which had the lowest Fe:S ratio, had the highest resultant H_2S production of 62 mL/kg of feedstock, whereas experiment I-1 with the highest Fe:S ratio had the lowest resultant H_2S production of 1.4 mL/kg of feedstock. The strikingly observed inconsistency between the modelled values and the experimental values in experiment II-2 was attributed to error propagation of the H_2S measurements, following the chosen experimental set-up. During the experiment, the gas was released after every measurement resulting in a pressure drop. According to Henry's law, H_2S has the highest Henry's constant of 0.1 mol/L*bar as compared to that of CO_2 and CH_4 , which are 0.031 mol/L*bar and 0.0016 mol/L*bar at standard temperature and pressure (Lindeboom, 2014). This implies that dissolved H_2S already produced migrates preferentially to the gas phase compared to CH_4 and CO_2 . Therefore, H_2S in subsequent measurements could be accounted for multiple times leading to an over estimation of the cumulative experimental H_2S production. On the other hand, the measured pH was 8.5 which was relatively high for bicarbonate-controlled alkalinity. Measurement errors in the pH, if propagated as model input, would lead to a 3-times under estimation of the modelled predicted H_2S if the actual reactor pH was 8, instead of the

recorded value of 8.5.

A similar trend was also observed comparing the measured results of urine and water dilution. When applying urine as diluent the resultant H_2S production from experiment 1, experiment II-1 and experiment II-2 was on average 51, 3 and 41 mL/kg of feedstock. Applying water as diluent resulted in an average Fe:S ratio in experiment I, experiment II-1 and experiment II-2 of 1:7.5, 1:0.6, 1:1.2 respectively. The Fe:S ratio was lowest in experiment I, having the highest average H_2S production of 41 mL/kg of manure followed by 4.4 mL/kg of manure and 18 mL/kg of manure in experiment II-1 and experiment II-2, respectively. It was further noted that reactors from experiment II-1 diluted with urine had relatively lower H_2S production than those diluted with water. This could be attributed to the higher pH of reactors diluted with urine as compared to those diluted with water. Contrary to this observation, reactors from experiment I and II-2 diluted with urine had higher H_2S production than reactors diluted with water. This, therefore, suggested that at a given pH, the metal elements:S ratio of the feed stock had a determining effect on the resultant H_2S in the biogas.

From Table 3, it follows that urine contains metal elements and sulphur. This implies that the use of urine instead of water as solvent adds extra sulphur and metal elements in the feedstock of the digester. However, if the metal element and sulphur content in feedstock diluted with urine has the ratio of metal element:S to less than 1:1, the use of urine as solvent instead of water is likely to increase the resultant H_2S content in the biogas.

The results of our present work show that the use of urine can greatly affect the equilibrium H_2S content in the biogas, influencing the composition of the biogas. Reduced H_2S content in the biogas could be attributed to the presence of metal elements in urine, such as Na, Fe, Mg etc. (Hindupur, 2018) and its relative high pH when it is hydrolysed. It is noteworthy that the chemical composition of urine could vary depending on the storage time, which can be attributed to hydrolysis of urea and other biochemical reactions, depending on conditions of storage (Miah et al., 2017). Notably, the NH_4^+ concentration will be higher leading to an increased pH if hydrolysed urine is used for dilution. The sulphate concentration in urine may exceed values of 250 mg S/L (Miah et al., 2017), which can increase the sulphur concentration in the feedstock and hence will increase the H_2S content in the biogas. However, in some cases, the S concentration in urine is less than 100 mg S/L. The variation in the urine S content is attributed to dietary intake (Devasena and Sangeetha, 2022). If urine with low sulphate concentration is used for dilution, while the metal content is high within cow dung and urine itself, a low H_2S content in the biogas is expected. Data presented in Table 4 show that experiments with a higher Fe:S ratio in the medium had a lower H_2S content in biogas, referring to reactors with urine dilution as compared to those with water dilution.

It is worth to note that urine may contain variable amounts of ammonia, sulphur and metals. At constant pH, high concentrations of sulphur will consequently increase the H_2S content in the biogas and high concentration of ammonia, and metal concentration in the feedstock can potentially inhibit the anaerobic digestion process. Therefore, if urine is to be used as an in-situ H_2S reduction method in the biogas, a proper balance between the additional sulphur load, and metal loads and the potential increase in pH is needed. It is also noteworthy that PhreeqC results are given under equilibrium conditions, which was, however, not the case for the batch-wise performed BSP experiments; for instance, in experiment I, a very low biogas production rate was observed indicating a non-stable digestion process. Therefore, further research under dynamic conditions is recommended.

In addition to the biogas H_2S content, urine also had a clear effect on the generated biogas quantity. In all experiments using 50% urine and 50% water dilution (urine:water 1:1), the biogas production was enhanced, which even exceeded the biogas production when 100% urine dilution was applied (Appendix 5, 9 and 10). Apparently, a proper urine to water dilution needs to be determined prior to use in anaerobic digestion.

4.2. The importance of predicting gaseous H₂S biogas content dynamics in continuous cow urine/ manure digestion

Modelling results using ADM1 to simulate the concentration of H₂S in the biogas using varying feedstock composition confirmed experimental results. While working at a comparable pH, a decreasing Fe:S ratio increased the resultant H₂S in the biogas. From field results in our previous research (Wasajja et al., 2021), it was observed that the frequency of feeding varies widely from one digester to the other. Such practices could result into varying biogas production rates and H₂S content. ADM1 modelling results in our present research indeed showed that inconsistency in feedstock composition and pattern resulted into a varying H₂S content. Although in practice, the H₂S pattern may not exactly follow the feedstock composition and pattern due to complexity of the AD process and physical properties such as mixing conditions in the reactor, ADM1 results showed that variable H₂S concentrations in the biogas can be expected. Therefore, when designing a cleaning system for H₂S, such variations should be considered. The kinetics of both H₂S and CH₄ production rates are likely to be feedstock dependent. Our present results showed that fluctuation in H₂S content in the biogas ranged between 100 ppm – 400 ppm, depending on the time of sampling. It is worth noting that specific cow urine and manure composition in terms of N and S-binding metal content needs to be determined to enable realistic predictions of field digester performance.

5. Conclusion

Experimental results showed that pH and trace metal elements influenced the H₂S content in the biogas of a manure digester. Results from experiments and modelling indicated that if urine is used with a high Fe:S ratio, i.e., greater than 1:0.5, the H₂S content in the biogas will be relatively low. Experimental data showed that cow urine contained metal elements and was characterised by a relatively high pH exceeding 7.7 when hydrolysed. A relatively high pH influenced the H₂S content by sulphur speciation, whereas metal elements reacted with S²⁻/HS⁻ to form metal sulphides. Therefore, the H₂S content in the biogas is determined by the total S content, the pH, and the Fe:S ratio. Results clearly showed that if urine is used as a solvent in biogas digester feed stock preparation, the biogas H₂S content is greatly affected. The overall effect of urine depends on the exact mineral urine composition and the composition of the used cow dung. If diluted feedstock with urine has a high Fe:S ratio, in-situ H₂S reduction in the evolving biogas is expected.

Therefore, if urine with low sulphur content and high metal content is used for dilution of digester feedstock, such that the overall Fe:S ratio is greater than 1:1, then the pH of feedstock will increase and in-situ H₂S reduction in biogas will be enhanced. Hence, in such case, urine dilution will be attractive for application in biogas-SOFC energy systems. However, if high-sulphur content urine is used, such that Fe:S ratio is less than 1:1, the usability of urine for in-situ H₂S biogas cleaning becomes less attractive.

CRediT authorship contribution statement

Henry Wasajja: Writing – original draft, Visualization, Methodology, Investigation, Conceptualization. **Ralph E.F. Lindeboom:** Writing – review & editing, Supervision, Project administration, Methodology, Conceptualization. **Henri Spanjers:** Writing – review & editing, Funding acquisition. **P.V. Aravind:** Writing – review & editing, Supervision, Funding acquisition. **Jules.B. van Lier:** Writing – review & editing, Supervision, Project administration, Methodology, Conceptualization.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biteb.2026.102546>.

Data availability

Data will be made available on request.

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