

REMOVING HYDROGEN SULPHIDE CONTAMINATION IN BIOGAS PRODUCED FROM ANIMAL WASTES

Cuong H Pham^{a, #}, Surinder Saggar^a, Peter Berben^a, Thilak Palmada^a, Craig Ross^a

^a*Mannaki Whenua - Landcare Research, Private Bag 11052, Palmerston North 4442, New Zealand*

[#] *On leave from: Ministry of Agriculture and Rural Development, National Institute of Animal Sciences, Hanoi 10000, Vietnam. Email: PhamC@landcareresearch.co.nz*

Abstract

Hydrogen sulphide (H₂S) contamination in biogas produced from animal wastes limits biogas use to cooking, resulting in release to the atmosphere of between 3 and 51% of total biogas produced. Biogas contains 50–70% methane, a potent greenhouse gas contributing to global warming. This study aimed to develop a cost-effective H₂S removal technology using local materials rich in iron that could be used to adsorb H₂S in a filtering system. Here we tested seven New Zealand soils at various gas flow rates. Among the soils used we found three soils (Allophanic soil, Brown soil, and Black sand) with high and stable H₂S removal efficiency (almost 100%) at all gas flow rates, followed by Typic sand (90–99%). Cheap filters to remove H₂S from biogas could potentially be made using local soils rich in iron. Regenerating iron oxide by simply exposing adsorption bed material to the atmosphere can improve H₂S removal efficiency.

Key words: H₂S removal; Biogas; Iron-rich soils; Gas flow rates

1. Introduction

Animal wastes have been widely used for small-scale energy production through anaerobic digestion in most of South-East Asia. Converting animal wastes to biogas is seen as a sustainable technology to supply renewable energy in developing countries such as India and Vietnam. However, sub-optimal management and utilization of biogas digester systems in these countries is a recognized source of air and water pollution (Vu, Q.D et al., 2012; Vu, T.K.V et al., 2007). Biogas produced from digesters is mainly used for cooking, but not for heating, lighting, and electricity generation (Thu et al., 2012), because the hydrogen sulphide (H₂S) content of biogas corrodes metal components in engines or gas burners (Hamilton, 1985; Muche and Zimmerman, 1985; Sommer et al., 2013; Sublette and Sylvester, 1987). Biogas produced in excess of that required for cooking (from 3 to 51% of total biogas produced) is intentionally released to the atmosphere (Bruun et al., 2014). There is a need to remove H₂S from biogas so that it can be used more widely, such as for energy generation, thereby limiting methane emissions from this technology.

Current technologies to purify biogas by removing H₂S use chemical liquids, membrane separation, biological filters, or activated carbon (Ryckebosch et al., 2011), which are not only costly and cumbersome to use but also result in low removal efficiencies. Lasocki et al. (2015) suggested testing locally sourced materials for use in H₂S adsorption beds. Using iron oxide (Fe₂O₃) rich material is a simple, efficient method to remove H₂S in biogas since iron oxide easily reacts with H₂S to form iron sulphide (Fe₂S₃) when biogas passes through it

(Zicari, 2003). However, soils rich in iron oxide, such as Brown soils that are available in tropical and sub-tropical climates throughout the world, have not been widely evaluated for their potential to remove H₂S from biogas. The objective of this study was to determine the potential of a number of locally available iron-rich New Zealand soils to remove H₂S from biogas to develop a simple, cost-effective, and sustainable technology for scrubbing biogas.

2. Materials and methods

2.1. Soil collection and preparation

The New Zealand Soil Survey Database was used to identify and locate sites representing soils rich in iron (Fe) (Table 1). In total, seven soils were identified as likely candidates for evaluation: Raw sand, Typic Sandy Brown Soil (Typic sand), Acidic Sandy Brown Soil (Acidic sand), Orthic Brown Soil (Brown soil), Orthic Podzol (Podzol soil), Orthic Allophanic Soil (Allophanic soil), and Black iron-sand (Black sand). The soils were sampled to 40-cm depth and, with the exception of Allophanic soil and Black sand, were sieved (2-mm sieve) and stored in plastic bags in a cold room (4°C to maintain moisture content). Black sand was sampled on the surface of the coastline; Allophanic soil was dried at room temperature and plant material removed before sieving and storing as above. The moisture content of the soils was determined by oven-drying the samples for 24 h at 105°C. Soil pH was measured in a 1:2.5 water suspension (Blakemore et al., 1987). Iron in the extract was determined by high-temperature emission spectroscopy using Microwave Plasma-Atomic Emission Spectroscopy technique (MP-AES).

Table 1. Soil Survey Database Information

No.	Soil types	Abbreviation	Location sites	Lat Long coordinates	Weight of soil in filters (g)
1	Raw sand	Raw sand	Peka Peka	175.060147E -40.830558S	2260
2	Acidic Sandy Brown Soil	Acidic sand	Te Horo	175.127761E -40.778815S	2600
3	Typic Sandy Brown Soil	Typic sand	Shannon	175.376932E -40.451773S	2600
4	Black iron-sand	Black sand	Tongaporutu	174.584037E -38.814919S	4100
5	Orthic Podzol	Podzol soil	Tangiwai	175.575922E -39.465544S	2040
6	Orthic Allophanic Soil	Allophanic soil	Stratford	174.304260E -39.335370S	1530
7	Orthic Brown Soil	Brown soil	Palmerston North	175.620606E -40.391196S	1750

2.2. Soil filter and H₂S removal process

A H₂S removal soil filter was made from a PVC plastic pipe (22 cm × 10 cm) with an air-tight screw cap at each end (Figure 1). An inlet port for introduction of H₂S gas was inserted at one end, and an outlet port to collect the treated gas was inserted at the other end. The filter consisted of a 2-cm gravel layer above the inlet port covered by a fine wire mesh and a Bidim A14 geotextile cloth to prevent blockage by the overlying filter material. The soil filters contained 1.5 l soil each (Table 1). Hydrogen sulphide in dinitrogen (N₂) at 2 concentrations – 3150 ppm (0.315±0.009%) and 5230 ppm (0.523±0.016%) (BOC, Australia) – was passed through the filter at flow rates of 59, 74, 94, 129 and 189 ml/min and at a constant pressure (100kPa) at room temperature (mean 19.5°C, maximum 22.7°C, minimum 15.6°C) for 4 h daily. Gas flow rate was controlled with a gas cylinder regulator (BOC, Australia) and a PTFE rotameter (Aalborg, USA). The reasons for the H₂S removal efficiency at flow rates of 74, 94 and 129 ml/min are not presented for Podzol soil, Black sand, Brown soil, and Allophanic soil with a 3150-ppm H₂S gas mixture; or for Raw sand, Typic sand, Black sand, and Allophanic soil with a 5230-ppm H₂S gas mixture (Table 3) because a similar decrease trend in H₂S removal with increasing gas flow rates was demonstrated by a 3150-ppm H₂S

gas mixture that passed through Raw sand, Acidic sand, and Typic sand. H₂S removal also reached nearly 100% by Allophanic soil, Black sand, and Brown soil at both gas flow rates of minimum and maximum (59 and 189 ml/min).

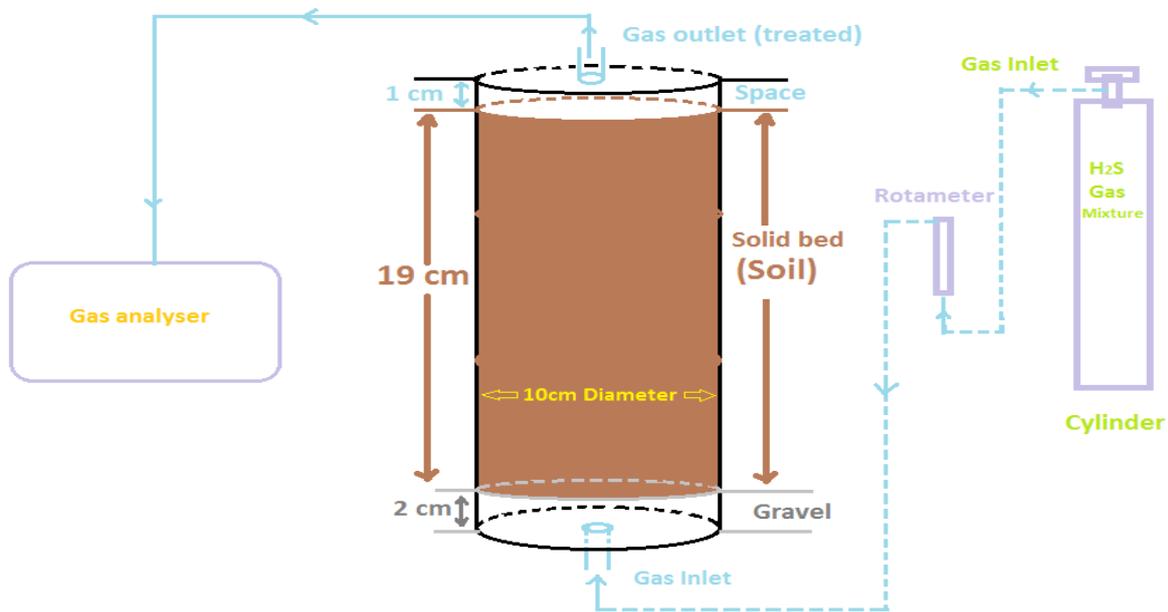


Figure 1. Diagram of H₂S removal process.

2.3. Iron oxide regeneration

An experiment to regenerate iron oxide (Fe₂O₃) by opening the soil filter then storing soil in plastic bags after finishing the filtration period was carried out with Typic sand and Black sand. A 5230-ppm H₂S gas concentration at a gas flow rate of 189 ml/min was passed through the soil filter with either Typic sand or Black sand for a 4-h feeding time in the first day (Day 0). The cap of the outlet port was then opened to see the colour of the soil, and also transfer Typic sand and Black sand into separate plastic bags for a 5- and 7-day storage respectively before continuing to feed a 5230-ppm H₂S gas concentration through these sand stored again (Day X).

2.4. H₂S Analyses

The H₂S concentration of treated gas at the outlet was analyzed at 15-min intervals for each flow rate; except for 59 ml/min flow rate, when outlet samples were analyzed at 30 min intervals. The gas from the outlet was collected in modified FoodSaver® bags for 15 or 30 min to obtain at least 1100 ml required for a 2-min stable H₂S concentration reading by the portable gas analyzer (GA5000 gas analyzer, Geotech, England) calibrated with a known standard H₂S concentration.

The H₂S removal efficiency (E) was calculated using equation 1:

$$E = ((I-O)/I)*100 \quad (\text{Eqn 1})$$

Where E is H₂S removal efficiency (%), I is soil filter gas concentration (ppm H₂S) at the inlet, O is soil filter gas concentration (ppm H₂S) at the outlet.

The gas retention time (GRT), which is the estimated time for which gas will be in contact with the soil in the H₂S adsorption filters, is mainly related to the porosity of the soils in the

1.5 l soil filter. The gas retention time at gas flow rates for each soil in Table 1 was calculated according to equation 2:

$$\text{GRT}=\text{V}/\text{GFR} \quad (\text{Eqn 2})$$

Where GRT is gas retention time (min), V is the pore volume of soil bed (l) (volume of soil bed (l) x porosity (%)), GFR is gas flow rate (l/min).

The porosity of the soils was calculated following equation 3:

$$P = (1-(B/D))\times 100 \quad (\text{Eqn 3})$$

Where P is porosity of soil (%), B is the bulk density of soil (g/cm³), D is the particle density of soil (g/cm³).

2.5. Data analysis

The H₂S removal efficiency (%) data were evaluated using analysis of variance (1-way ANOVA) followed by the Ryan-Einot-Gabriel-Welsch multiple-range test where appropriate (SAS 9.2 TS Level 2M0, SAS Institute Inc., Cary, NC, USA). In all cases, a significance level of $\alpha = 0.05$ was used. When necessary, data were transformed (log₁₀) to obtain normality and homogeneity of variances (Zar, 1984).

3. Results and discussion

3.1. Soil characteristics

The soil pH, iron content, moisture content, and porosity of the soils are presented in Table 2. Soil pH was the lowest for Podzol soil (4.37), intermediate for Brown soil, Acidic sand and Raw sand (5.42 – 5.87), and highest for Typic sand, Black sand and Allophanic soil (6.31 – 6.52). Porosity ranged between 38.1 and 46.7% for sand soils, but increased to 73.6 – 83.9% for non-sand soils. Moisture content of soils was from 6.6 to 22.4%, apart from Black sand, which had a moisture content of less than 1. Iron content was the lowest for Raw sand, Acidic sand, and Podzol soil (about 1%), was slightly greater for Brown soil and Typic sand (<2%) and Allophanic soil (4%), and highest for Black sand (42%). Gas retention time was from 3.0 to 11.8 min for sand soils, but increased up between 5.8 and 21.1 min for non-sand soils.

Table 2. Characteristics of local materials

	Raw sand	Acidic sand	Typic sand	Black sand	Podzol soil	Allophanic soil	Brown soil
pH	5.9	5.4	6.5	6.3	4.4	6.4	5.7
Porosity, %	46.7	42.3	44.0	38.1	73.6	74.8	83.9
Moisture, %	6.6	11.9	13.5	0.1	10.1	10.2	22.4
Iron, %	1.3	1.3	1.7	41.8	0.9	4.1	1.7
Gas flow rate (ml/min)	Gas retention time (min)						
59	11.8	10.6	11.1	9.6	18.5	18.8	21.1
74	9.5	8.5	8.9	7.7	14.9	15.1	17.0
94	7.4	6.7	7.0	6.1	11.7	11.9	13.4
129	5.4	4.9	5.1	4.4	8.5	8.7	9.7
189	3.7	3.3	3.5	3.0	5.8	5.9	6.6

3.2. H₂S removal efficiency

3.2.1. Effect of gas flow rates

Table 3. H₂S removal efficiency (%) by gas flow rates and local materials over 4 h

Gas flow rates (ml/min)	Local materials						
	Raw sand	Acidic sand	Typic sand	Podzol soil	Black sand	Brown soil	Allophanic soil
<i>3150 ppm H₂S gas mixture</i>							
59	99.1 ^a	88.7 ^a	99.1 ^a	86.9 ^a	100	100	100
74	98.4 ^a	81.2 ^a	98.2 ^{ab}	ND	ND	ND	ND
94	95.8 ^{ab}	68.7 ^b	97.2 ^b	ND	ND	ND	ND
129	89.8 ^b	60.8 ^b	94.2 ^c	ND	ND	ND	ND
189	75.7 ^c	47.5 ^c	88.6 ^d	57.7 ^b	99.7	99.3	100
Mean	91.4 ^B	67.2 ^C	95.1 ^{AB}	67.5 ^C	99.8 ^A	99.5 ^A	100 ^A
<i>5230 ppm H₂S gas mixture</i>							
59	89.3 ^a		98.7 ^a		100		ND
189	57.5 ^b		93.8 ^b		93.1		100
Mean	68.1 ^B		95.4 ^B		95.4 ^A		100 ^A

^{a,b,c,d}Means in the same column for each material with different superscripts are significantly different ($P < 0.05$).

^{A,B,C}Means of each material in the same row with different superscripts are significantly different ($P < 0.05$).

ND, not determined.

The results of H₂S removal efficiency (%) of each soil filter during 4 h feeding time are presented in Table 3. The Allophanic soil, Black sand, and Brown soil removed almost 100% of H₂S at the gas flow rates tested, while Typic sand removed 90–99%. There was a significant decrease in H₂S removal after 120-min feeding at 189 ml/min flow rate for 5230-ppm H₂S gas for Black sand only (Figure 2). These results are in agreement with the studies of Chung et al. (2006), who concluded that more than 99.5% of H₂S is removed in the first 10 h of feeding by chemical adsorption, Lasocki et al. (2015), who indicated that using bog iron ore and activated carbon as H₂S adsorption beds in filters also reduced almost 100% of H₂S in a 30-min exposure period, and Rogers and Whitehead (1998), who showed that 2500-ppm H₂S concentration in raw gas was removed to below 1 ppm by three different filtration stages including an iron chelate solution, a dry iron oxide box, and an activated carbon filter. In our study, the H₂S removal efficiency dropped considerably with increasing feeding time, irrespective of the flow rates for Raw sand, Acidic sand, and Podzol soil (Figure 3). These are similar trends to the previous studies of Lien et al. (2014), who indicated that H₂S removal efficiency dropped dramatically with an increase in the water scrubbing time (min) from 80% in the first min to a few percent after 6 min. Chung et al. (2006) showed that there was a decrease in H₂S removal efficiency with increasing feeding time (h) of the chemical adsorption reactor.

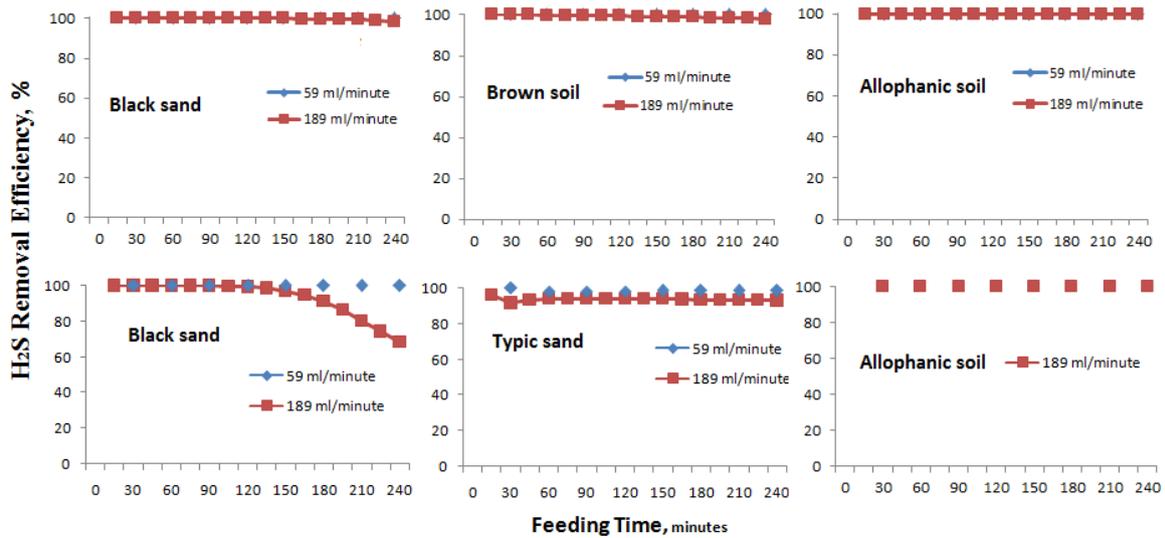


Figure 2. H₂S removal at 3150 ppm (top row) and 5230 ppm (bottom row) H₂S gas mixture.

Although there was not a significant difference in H₂S removal efficiency between minimum and maximum gas flow rates for Black sand, Allophanic soil, and Brown soil, the H₂S removal efficiency of Raw sand, Acidic sand, Typic sand, and Podzol soil increased with reduced gas flow rates (i.e. increased retention time). These results are in agreement with previous studies (Chung et al., 2006; Ho et al., 2013; Horikawa et al., 2004; Lin et al., 2013), which removed H₂S by a combined chemical-biological solution, showing that H₂S removal efficiency increased with increasing retention time. Others have found that H₂S removal efficiency increased with increasing retention time through increasing bed height of bog iron ore (30, 53, and 80 mm height) at the same gas flow rate (Lasocki et al., 2015); or with decreasing biogas flow rates (from 60–80% at 50 l/min to 25–60% at 140 l/min) (Lien et al., 2014). Pagella et al. (1996) found that the H₂S removal efficiency can be enhanced through either reducing gas flow rates or increasing the soil volume.

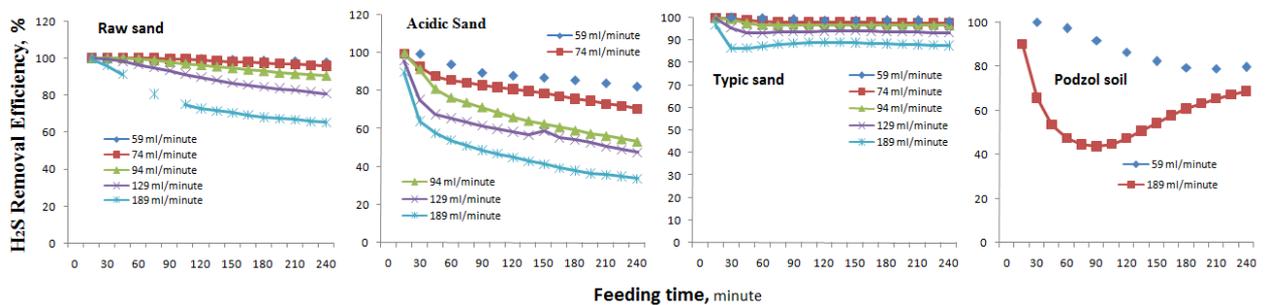


Figure 3. H₂S removal for inlet 3150-ppm H₂S gas mixture.

3.2.2. Soil effects

The mean H₂S removal efficiency of each soil during 4 h of feeding time presented in Table 3 indicated there was a significant difference in H₂S removal efficiency between materials at both 3150- and 5230-ppm H₂S gas mixtures. For the 3150-ppm H₂S gas mixture, the H₂S removal efficiency achieved around 99% for Allophanic soil, Brown soil, and Black sand, then slightly decreased to 95% for Typic sand, 91% for Raw sand, and was the lowest for Podzol soil and Acidic sand at about 67%. Similarly, the H₂S removal efficiency for 5230-

ppm H₂S gas mixture was the highest for Allophanic soil (99%), followed by Black sand and Typic sand (95%), and lowest for Raw sand (68%). The reason for this significant difference in H₂S removal among the soils may be because of the form and content of iron (Fe) in the soils. As iron generally remains in hydrated iron oxide form in Brown soil, Allophanic soil, and other iron sands, we expect that the iron oxide (Fe₂O₃) in these soils would readily react with hydrogen sulphide (H₂S) to form iron sulphide (Fe₂S₃) and water (H₂O) when the gas mixtures passed through the soil filters (Dillon, 1990). McLaren and Cameron (1996) showed that iron oxides that were usually found in tropical and sub-tropical soils were magnetite Fe₃O₄ (FeO/Fe₂O₃, black), hematite α -Fe₂O₃ (red), and maghemite γ -Fe₂O₃ (reddish brown). In addition, Allophanic brown soils and Sandy brown soils are two groups of Brown soils that normally include 2:1 clay minerals and secondary iron oxides.

Previous studies on soils in New Zealand indicated that Loamy sand contained 0.1 – 1.45% Fe, 0.1 – 1.5% Fe₂O₃ (Luke, 1968b). In the A2 Horizon of Podzols soil, Zonal soils and Intrazonal soils the iron contents were 0.6 – 2.5%, 0.01 – 1.97% and 0.22 – 3.7% respectively (Luke, 1968a). Allophane samples contained 0.1 to 3.5% iron (Theng et al., 1982); and a Black iron-sand contained about 58–60% iron (Wylde, 1918). The iron content of soils used in this study is shown in Table 2. As a result, the H₂S removal efficiency was much greater for soils with high iron content (1.65 – 41.83%) than for soils with low iron content (0.89 – 1.33%). However, H₂S removal efficiency quickly dropped after 120 min of feeding 5230-ppm H₂S gas mixture for Black sand that contained high iron content (42%). Low moisture content in Black sand (0.07%) may be the main reason for this reduction of H₂S removal efficiency, because the iron oxide needs to be maintained in a moist state to ensure the iron remained in the hydrated form (Anerousis and Whitman, 1985). This moisture content problem can be dealt with since real biogas contains 5–10% water (Ryckebosch et al., 2011).

Furthermore, the soil texture and porosity may be involved in the different H₂S removal efficiency between soil types because there are significantly more reactivity surfaces per unit of volume in a soil with reasonable clay content compared with a sand or loamy sand soil. In the present study the porosity was higher for soils (74–84%) than for sand categories (38–47%), similar to previous studies (30–46% for sand, 70–84% for soils) (McLaren and Cameron, 1996; Prochaska and Zouboulis, 2003; Rolland et al., 2009; Pratt et al., 2012, 2013; Tate et al., 2012).

3.3. *The longevity of H₂S removal*

The H₂S removal efficiency of Typic sand and Allophanic soil still remained stable at around 90% to 100% for over 4 h of feeding time in Figures 2 and 3. A 5230-ppm H₂S gas was then used to pass through Typic sand and Allophanic sand for 4 h per day at a gas flow rate of 189 ml/min until H₂S removal was significantly reduced to help understand the sustainability and longevity of H₂S removal (Figure 4). The results showed that the H₂S removal efficiency started to drop after a few min for raw sand, after 150 min for Black sand, but still stayed at about 90% after 2 feeding days for Typic sand, and remained at nearly 100% after more than 4 feeding days for Allophanic soil. This finding could be used to estimate both the time (h) to replace the new soils, and the time (h) needed to regenerate iron oxide by allowing air into the soil filters. In addition, the sustainability and longevity of H₂S removal efficiency may be extended through regenerating iron oxide as described in the following section.

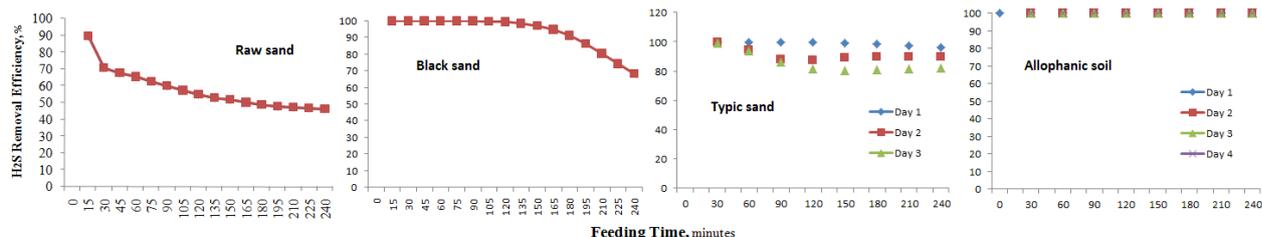
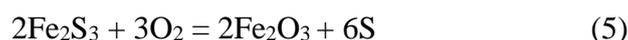
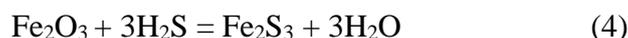


Figure 4. The longevity of H₂S removal efficiency.

3.4. Iron oxide regeneration

The results showed that the H₂S removal efficiency (%) had a higher trend for Day X (air mixed) than for Day 0 for both Typic sand and Black sand. The mean value (standard deviation) of H₂S removal efficiency was 93.80% (0.90) for Day 0, but increased to 98.82% (1.37) for Day X ($P < 0.0001$) for Typic sand. This significant difference plays an important role not only in enhancing the H₂S efficiency, but also in re-using these local materials for a longer H₂S removal period. In addition, the colour of Typic sand was brown (iron oxide (Fe₂O₃) colour in soil) (McLaren and Cameron, 1996) early in Day 0 (before feeding a H₂S gas mixture), but changed to black (iron sulphide colour) after 4 h of feeding time late in Day 0. However, its colour reverted to brown (original colour) in Day X after sand was mixed with air and stored in plastic bags for 5 and 7 days respectively for Typic sand and Black sand. This is in agreement with the H₂S chemical removal mechanism, indicating that H₂S in gas reacts with iron oxide in soil to form iron sulphide and water (equation 4). Then iron oxide can be regenerated by supplying air (O₂) over the soil filters through a reaction between iron sulphide and oxygen (equation 5) (Krich et al., 2005). This finding can be applied to regenerate iron oxide by running an open H₂S filtration system instead of the closed biogas utilization system, as is presently used in some countries like Vietnam (Nguyen et al., 2010). This also means that both the inlet and outlet ports of the soil filter need to be opened to allow air into the filter after the H₂S removal process.



4. Conclusions

The H₂S removal efficiency was almost 100% at all gas flow rates for Allophanic soil, Brown soil and Black sand, followed by Typic sand (around 90–100%). Our study showed that a selection of New Zealand soils with high iron content could potentially be used to construct simple and inexpensive H₂S adsorption beds to enhance biogas quality. The H₂S removal efficiency of used soil materials can be improved by exposing them to the atmosphere.

Acknowledgments

The Senior author Post-Doctoral was funded by the New Zealand Government Livestock Emissions and Abatement Research Network (LEARN) and supported by Manaaki Whenua Landcare Research. Thanks to John Dando, Harley Betts, Paul Peterson, Ngaire Foster for technical support, Anne Austin for editing, and Dr Jeyakumar, Massey University, NZ for iron analysis.

References

1. Anerousis, J.P., Whitman, S.K., 1985. Iron sponge: still a top option for sour gas sweetening. *OIL GAS J.* 83, 71–76.
2. Bruun, S., Jensen, L.S., Vu, T.K.V., Sommer, S.G., 2014. Small-scale household biogas digesters: An option for global warming mitigation or a potential climate bomb? *Renew. Sust. Energy Rev.* 33, 736–741.
3. Blakemore, L.C., Searle, P.L., Daly, B.K., 1987. Methods for chemical analysis of soils. New Zealand Soil Bureau Scientific Report 80. New Zealand Soils Bureau, Lower Hutt.
4. Chung, Y., Ho, K., Tseng, C., 2006. Treatment of High H₂S Concentrations by Chemical Absorption and Biological Oxidation Process. *Environ. Eng. Sci.* 23, 942–953.
5. Dillon, E.T., 1990. Composition and Method for Sweetening Hydrocarbons. Conshohocken, PA, U.S, Quaker Chemical Corporation.
6. Hamilton, W.A., 1985. Sulphate-reducing bacteria and anaerobic corrosion. *Annual Review of Microbiology.* 39, 195–217.
7. Ho, K., Lin, W., Chung, Y., Chen, Y., Tseng, C., 2013. Elimination of high concentration hydrogen sulfide and biogas purification by chemical–biological process. *Chemosphere.* 92, 1396–1401.
8. Horikawa, M.S., Rossi, F., Gimenes, M.L., Costa, C.M.M., Silva, M.G.C., 2004. Chemical absorption of H₂S for biogas purification. *Braz. J. Chem. Eng.* 21, 415–422.
9. Krich, K., Augenstein, A., Batmale, J., Benemann, J., Rutledge, B., Salour, D., 2005. Upgrading dairy biogas to biomethane and other fuels. In: Andrews K. (Ed.), *Biomethane from Dairy Waste: A Sourcebook for the Production and Use of Renewable Natural Gas in California.* Clear Concepts, California, pp. 47–69.
10. Lasocki, J., Kolodziejczyk, K., Matuszewska, A., 2015. Laboratory-scale investigation of biogas treatment by removal of hydrogen sulfide and carbon dioxide. *Pol. J. Environ. Stud.* 24, 1427–1434.
11. Lin, W., Chen, Y., Tseng, C., 2013. Pilot-scale chemical–biological system for efficient H₂S removal from biogas. *Bioresour Technol.* 135, 283–291.
12. Lien, C.C., Lin, J.L., Ting, C.H., 2014. Water scrubbing for removal of hydrogen sulphide (H₂S) Nibio gas from Hog Farms. *J Agric Chem Environ.* 3, 1–6.
13. Luke, J., 1968a. N.Z. Soil Bureau 1968: Soils of New Zealand Part 2. N.Z. Soil Bur. Bull. 26.
14. Luke, J., 1968b. N.Z. Soil Bureau 1968: Soils of New Zealand Part 3. N.Z. Soil Bur. Bull. 26.
15. McLaren, R.G., Cameron, K.C., 1996. Soil science: Sustainable production and environmental protection. Oxford University Press, Auckland, New Zealand.
16. Muche, H., Zimmerman, H., 1985. Purification of Biogas. Friedr. Vieweg & Sohn.
17. Nguyen, D.L., Nguyen, T.K., Nguyen, K.Q., 2010. Questions and Answers about Biogas Technologies. Vietnam Agric. Publishing House, Hanoi, Vietnam.
18. Pratt, C., Deslippe, J., Tate, K.R., 2013. Testing a biofilter cover design to mitigate dairy effluent pond methane emissions. *Environ. Sci. Technol.* 47, 526–532.

19. Pratt, C., Walcroft, A.S., Tate, K.R., Ross, D.J., Roy, R., Reid, M.H., Veiga, P.W., 2012. Biofiltration of methane emissions from a dairy farm effluent pond. *Agric. Ecosyst. Environ.* 152, 33–39.
20. Prochaska, C.A., Zouboulis, A.I., 2003. Performance of intermittently operated sand filters: a comparable study treating wastewaters of different origins. *J. Environ. Manage.* 147, 367–388.
21. Pagella, C., Silvestri, P., De Faveri, D.M., 1996. H₂S gas treatment with *Thiobacillus ferrooxidans*: Overall process performance and the chemical step. *Trans IchemE.* 74, 123–132.
22. Ryckebosch, E., Drouillon, M., Vervaeren, H., 2011. Techniques for transformation of biogas to biomethane. *Biomass Bioenergy.* 35, 1633–1645.
23. Rolland, L., Molle, P., Liénard, A., Bouteldja, F., Grasmick, A., 2009. Influence of the physical and mechanical characteristics of sands on the hydraulic and biological behaviors of sand filters. *Desalination.* 248, 998–1007.
24. Rogers, G.N.D., Whitehead, A., 1998. Design of a three-stage filtration system to remove contamination Sulphur compounds from a CO₂-enriched gas supply for use in long-term tree growth experiments. *Environ Technol.* 19, 103–107.
25. Sublette, K.L., Sylvester, N.D., 1987. Oxidation of hydrogen sulfide by *Thiobacillus denitrificans*: desulfurization of natural gas. *Biotech. Bioeng.* 29, 249–257.
26. Sommer, S.G., Christensen, L.M., Schmidt, T., Lars, J.S., eds. 2013. *Animal Manure: Recycling, Treatment, and Management.* John Wiley & Sons, Chichester, United Kingdom.
27. Tate, K.R., Walcroft, A.S., Pratt, C., 2012. Varying atmospheric methane concentrations affect soil methane oxidation rates and methanotroph populations in pasture, an adjacent pine forest, and a landfill. *Soil Biol Biochem.* 52, 75–81.
28. Theng, B.K.G., Russell, M., Churchman, G.J., Parfitt, R.L., 1982. Surface properties of allophane, halloysite, and imogolite. *Clays and Clay Minerals.* 30, 143–149.
29. Thu, C.T.T., Cuong, P.H., Hang, L.T., Chao, N.V., Anh, L.X., Trach, N.X., Sommer, S.G., 2012. Manure management practices on biogas and non-biogas pig farms in developing countries using livestock farms in Vietnam as an example. *J. Cleaner Prod.* 27, 64–71.
30. Vu, T.K.V., Tran, M.T., Dang, T.T.S., 2007. A survey of manure management on pig farms in Northern Vietnam. *Livest. Sci.* 112, 288–297.
31. Vu, Q.D., Nguyen D.P., Vu T.K.V., Tran M.T., Vu C.C., Lars S.J., 2012. Effect of biogas technology on nutrient flows for small- and medium-scale pig farms in Vietnam. *Nutr Cycl Agroecosyst.* 94, 1–13.
32. Wylde, A., 1918. Technological innovation and economic growth in New Zealand: 1918 to “Think Big”. Available from: <http://www.techhistory.co.nz/IronSands/Titanium.htm>.
33. Zicari, S.M., 2003. Removal of hydrogen sulfide from biogas using cow-manure compost. Department of biological and Environmental Engineering, Master of Science, Cornell, Ithaca.
34. Zar, J.H., 1984. *Biostatistical Analysis*, 2nd edn. Prentice-Hall, Englewood Cliffs, NJ, USA.