Bioresource Technology 173 (2014) 443–447

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Short Communication

Oxidation reduction potential as a parameter to regulate micro-oxygen injection into anaerobic digester for reducing hydrogen sulphide concentration in biogas

Long D. Nghiem [a,*], Patrick Manassa [a], Marcia Dawson [b], Shona K. Fitzgerald [b]

[a] Strategic Water Infrastructure Laboratory, School of Civil Mining and Environmental Engineering, University of Wollongong, Wollongong, NSW 2522, Australia
[b] Sydney Water Corporation, Parramatta, NSW 2124, Australia

HIGHLIGHTS

- Micro oxygen injection to an anaerobic digester can reduce H_2S in biogas.
- ORP can be used as the regulating parameter to control oxygen injection.
- H_2S in biogas as low as 30 ppm was obtained at ORP in the range of −320 to −270 mV.
- Micro oxygen injection did not negatively affect anaerobic digestion.
- Using ORP to regulate oxygen injection could be readily implemented at full scale.

ARTICLE INFO

Article history:
Received 9 July 2014
Received in revised form 10 September 2014
Accepted 11 September 2014
Available online 18 September 2014

Keywords:
Anaerobic digestion
Micro-aeration
Hydrogen sulphide
Biogas
Oxidation reduction potential (ORP)

ABSTRACT

This study aims to evaluate the use of oxidation reduction potential (ORP) to regulate the injection of a small amount of oxygen into an anaerobic digester for reducing H_2S concentration in biogas. The results confirm that micro-oxygen injection can be effective for controlling H_2S formation during anaerobic digestion without disturbing the performance of the digester. Biogas production, composition, and the removal of volatile solids (VS) and chemical oxygen demand (COD) were monitored to assessment the digester's performance. Six days after the start of the micro-oxygen injection, the ORP values increased to between −320 and −270 mV, from the natural baseline value of −485 mV. Over the same period the H_2S concentration in the biogas decreased from over 6000 ppm to just 30 ppm. No discernible changes in the VS and COD removal rates, pH and alkalinity of the digestate or in the biogas production or composition were observed.

1. Introduction

Anaerobic digestion is the most widely used technique for treating sewage sludge in medium and large wastewater treatment plants (Brisolara and Qi, 2013; Jenicek et al., 2012, 2010; Wang et al., 2013). Anaerobic digestion is also widely used for the treatment of organic waste materials such as agro-waste and the putrescible fraction of municipal solid wastes (Karthikeyan and Visvanathan, 2013). During anaerobic treatment, organic materials in the sludge are transformed to biogas which comprises mostly methane and carbon dioxide. During this process, substantial reductions in the quantity of pathogenic organisms can be achieved. As readily biodegradable solids, known as volatile solids (VS), are substantially removed by anaerobic digestion, the final product is stable and can be suitable for agricultural use (Brisolara and Qi, 2013). If captured, the biogas produced from anaerobic digestion is a form of renewable fuel and can be used for heat and electricity generation to off-set the energy input into wastewater treatment (Jenicek et al., 2012).

During anaerobic digestion, sulphur is reduced to hydrogen sulphide (H_2S). In general, H_2S concentration in biogas obtained from the anaerobic digestion of wastewater sludge is in the range between 1000 and 2400 ppm. H_2S concentrations of up to 10,000 ppm have also been reported in some cases (Wellinger and Linberg, 2000). The occurrence of H_2S in biogas can significantly reduce its economic value and reuse potential because oxidised sulphur compounds can be very corrosive in the presence of water. H_2S is also extremely reactive with most metals and the reactivity can be increased by pressure, temperature, and the

* Corresponding author. Tel.: +61 2 4221 4590.
E-mail address: longn@uow.edu.au (L.D. Nghiem).

http://dx.doi.org/10.1016/j.biortech.2014.09.052
0960-8524/

presence of water. Therefore, before biogas can be used H_2S must be removed or at least reduced to minimise corrosion in compressors, gas storage tanks and engines (Wellinger and Linberg, 2000).

In practice, H_2S removal from biogas has been achieved by various physical, chemical and biological processes. These include the use of dry or wet adsorbent (also known as dry or wet scrubbing), membrane separation, chemical precipitation using metal salts (such as iron chloride) and biological scrubbing. However, these types of post-treatment of biogas to remove H_2S can be energy intensive and expensive. The cost of replacing the adsorbent 'scrubbing' media in a typical wastewater treatment plant of about 50 ML/d in capacity to achieve a H_2S concentration in biogas of less than 400 ppm is around AU$100,000 a year.

Given the high cost of post-treatment H_2S removal, there has been a significant research interest to develop in-situ techniques to control and reduce the formation of H_2S during the digestion process. A notable technique that could cost-effectively reduce H_2S formation and hence concentration of H_2S in biogas is micro-aeration (Díaz et al., 2011a,b,c, 2010; Díaz and Fdz-Polanco, 2012; Duangmanee, 2009; Fdz.-Polanco et al., 2009; Khanal and Huang, 2006).

Micro-aeration is the controlled introduction of a minute amount of oxygen or air into an anaerobic digester while maintaining anaerobic conditions. This enables anaerobic digestion of organic waste to continue while reducing the potential for H_2S formation. The effectiveness of micro-aeration for controlling H_2S in biogas has been demonstrated by a number of laboratory scale investigations (Díaz et al., 2011a,b,c, 2010; Díaz and Fdz-Polanco, 2012; Duangmanee, 2009; Fdz.-Polanco et al., 2009; Khanal and Huang, 2006). Short term full scale demonstration of micro-aeration to reduce H_2S concentration in biogas has also been reported (Jenicek et al., 2008). Micro-aeration can oxidise H_2S to elementary sulphur or prevent the reduction of sulphur into H_2S.

The oxidisation of H_2S to elementary sulphur utilises a consortium of sulphur-oxidising microorganisms such as *Thiobacillus* to oxidise sulphide to elementary sulphur. These sulphur-oxidising microorganisms are ubiquitously present in anaerobic digestion, so their inoculation to the system is not required (Wellinger and Linberg, 2000). As most of them are autotrophic, they can use the carbon dioxide in biogas as a carbon source (Wellinger and Linberg, 2000). Hence they have the potential to improve production rate and composition of biogas from anaerobic digestion.

It has also been suggested that the reduction of sulphur into H_2S is prohibited under a micro-aeration condition. Indeed, there exists a redox potential window that is inhibitory to the formation of H_2S but not CH_4. The oxidation reduction potential (ORP) is a measure of the redox potential and is sensitive to the presence of O_2 in an aqueous solution. Thus, ORP can be used to define the condition of biochemical reactions. The optimum ORP for CH_4 reducing bacteria is below −230 mV while an ORP value above −280 mV is inhibitory to sulphate reducing bacteria (Duangmanee, 2009; Hungate, 1969).

Although it is still not clear which of the two above mentioned mechanisms is dominant, both requires the introduction of a minute amount of oxygen (O_2) to the digester. However, introducing oxygen into an anaerobic environment is risky both from safety and digester performance perspectives. Thus, in this study, we propose to use ORP to regulate the oxygen injection to create a micro-aeration condition for controlling H_2S formation. It is also noted that while the effectiveness of micro-oxygen injection aeration to reduce H_2S concentration in biogas has been confirmed by many laboratory scale studies, practical demonstration of this approach at pilot or full scale level has not been demonstrated.

A review of literature, suggests that all previous studies, except one (Khanal and Huang, 2006), have relied on the O_2 to S^{2-} molar ratio or the H_2S concentration in biogas to determine the volume of O_2 to be injected into the digester. Our literature review indicates that the optimum O_2 to S^{2-} molar ratio is between 0.3 and 1.0 (Duangmanee, 2009). In a recent study, Ramos and Fdz-Polanco (2014) have successfully used the H_2S concentration in biogas (measured by a micro GC) to control the rate of O_2 injection. However, both of these methods are not practical because O_2 over loading can disrupt the anaerobic process. Therefore, this study aim to develop and trial a technique that can be readily retrofitted into an existing plant to reduce H_2S concentration in biogas using controlled oxygen injection.

2. Methods

2.1. Anaerobic digesters

Two anaerobic digesters were used in parallel. Each digester consisted of an anaerobic reactor, a mechanical mixer, feed and circulation pumps and a gas holder. The active volume of the reactor was 50 L with a head space of about 20 L. A Supervisory Control and Data Acquisition (SCADA) system was used to control both digesters. A detailed description of these anaerobic digesters is available elsewhere (Nghiem et al., 2014). ORP was measured using an ORP probe inserted into the anaerobic reactor just below the sludge level. This probe was connected to the SCADA system for data acquisition and system control. In this study, Digester 1 was chosen as the control, while Digester 2 was used for evaluating the micro-oxygen injection. Apart from additional oxygen injection equipment to Digester 2, both experimental systems were identical. Oxygen injection equipment attached to Digester 2 included an oxygen bottle with a flow regulator, an electrically actuated ball valve and an oxygen diffuser. Oxygen was supplied to the diffuser from a pressurised oxygen bottle via an electrically actuated ball valve. The ball valve opened or closed according to signal from the SCADA system to maintain the ORP level between −310 and −290 mV. A schematic diagram of digester 2 is shown in Fig. 1.

2.2. Monitoring and measurement

Biogas flow rate, digester temperature, ORP, and pressure were monitored in real time and recorded by the SCADA system. Biogas composition (CH_4, CO_2, H_2S, and O_2) was measured daily using a portable biogas analyser (Biogas 5000, Geotech, UK). The gas holder was emptied at the end of each working day. Biogas is allowed to accumulate in the gas holder overnight and one litre biogas sample was taken for analysis at the beginning of the following day. Total solids (TS), volatile solids (VS), chemical oxygen

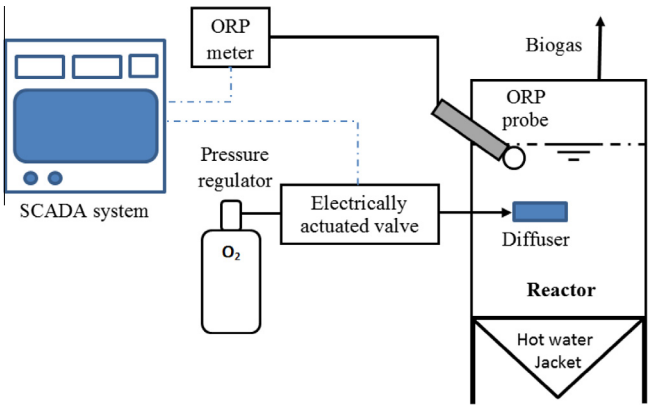

Fig. 1. Schematic diagram of digester 2 with additional equipment for micro-aeration.