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Development and validation of a simplified titration method for monitoring volatile fatty acids in anaerobic digestion

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ABSTRACT

The volatile fatty acids (VFAs) concentration has been considered as one of the most sensitive process performance indicators in anaerobic digestion (AD) process. However, the accurate determination of VFAs concentration in AD processes normally requires advanced equipment and complex pretreatment procedures. A simplified method with fewer sample pretreatment procedures and improved accuracy is greatly needed, particularly for on-site application. This report outlines improvements to the Nordmann method, one of the most popular titrations used for VFA monitoring. The influence of ion and solid interfering subsystems in titrated samples on results accuracy was discussed. The total solid content in titrated samples was the main factor affecting accuracy in VFA monitoring. Moreover, a high linear correlation was established between the total solids contents and VFA measurement differences between the traditional Nordmann equation and gas chromatography (GC). Accordingly, a simplified titration method was developed and validated using a semi-continuous experiment of chicken manure anaerobic digestion with various organic loading rates. The good fitting of the results obtained by this method in comparison with GC results strongly supported the potential application of this method to VFA monitoring.

1. Introduction

Anaerobic digestion (AD) is a complex series of biological processes, and has attracted worldwide attention owing to its ability to treat various types of organic wastes in a robust and efficient manner, while simultaneously producing bio-energy in the form of methane (Lauwers et al., 2013; Madsen et al., 2011; Zhang et al., 2014). Although AD technology has been investigated for several decades, poor performance and fermentation failure are still frequently reported, mainly due to insufficient operational management and lack of process monitoring and control (Khan and Martin, 2016; Labatut and Gooch, 2012; Williams et al., 2013). A few modern industrial bio-digesters can be continuously monitored online, but the limited measurable parameters, including pH, temperature, production, and composition of resultant gas, which, in most cases are insufficient to trigger the warning alarm fast enough to prevent system failure. In China, for example, the number of medium and large-scale biogas plants with monomer volumes of more than 300 m^3 has increased from 13,667 in 2011 to 15,531 in 2013 (Chen, 2014). However, long-term, the prompt and efficient follow-up services, like routine monitoring, are still insufficient in China, currently. As a result, the majority of these biogas plants are run at relatively low organic loading rates (OLR) (around 1–3 kg VS $(m^3 \cdot d)^{-1}$) as a safety precaution (De Neve and Lievens, 2004). Therefore, in order to improve the AD efficiency and stability, and achieve successful operation of anaerobic treatment facilities, reasonably accurate and rapid monitoring techniques are essential (Labatut and Gooch, 2012).

VFAs are important intermediates and metabolites and their concentration will change in response to operating parameters suddenly change or inhibitors occur (Mechichi and Sayadi, 2005). The accumulation of VFAs could be inhibitory and indicative of a kinetic uncoupling between acids producers and consumers, which is typical for stress situations (Ahring et al., 1995). Thus VFAs concentration has been widely accepted as a sensitive and reliable indicator for AD processes monitoring (Ahring et al., 1995; Boe et al., 2010; Lützhøft et al., 2014). In AD with agriculture resources, such as pig manure and chicken manure that rich in nitrogen and easily biodegradable organic compounds, VFAs accumulation occurred as a result of ammonia inhibition often causes system failure (Zhang et al., 2017). High total solids in feedstock for AD with various types of manure is typical which aggravate the possibility in generating inhibitors of methanogenesis, such as excessive VFAs, during the AD process (Ward et al., 2008). Currently, a

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variety of methods have been previously reported for VFAs quantitative measurement, and the most common used methods mainly including titration (Lahav and Morgan, 2004; Moosbrugger et al., 1993b; Zaher et al., 2004), gas or liquid chromatography (Boe et al., 2007; Cruwys et al., 2002; Peu et al., 2004), and spectroscopy (Jacobi et al., 2011; Krapf et al., 2013; Steyer et al., 2002). For routine monitoring and control, the titrimetric technique is generally accepted to be superior in simplicity, speediness, robustness, and cost-effectiveness compared with other methods. Furthermore, it has the advantage of being able to measure alkalinity and VFA concentrations simultaneously (Hey et al., 2013; Mota et al., 2015).

In recent decades, various titration methods have been developed and validated for measuring VFA concentrations in the AD process to a certain degree of accuracy (Lahav and Morgan, 2004; Moosbrugger et al., 1993b), e.g. 2 pH-point methods (Anderson and Yang, 1992; Nordmann, 1977), 4 pH-points methods (Moosbrugger et al., 1993c, 1993d), 5 pH-point method (Moosbrugger et al., 1993a), 8 pH-point method (Lahav et al., 2002), and 9 pH-point (Ai et al., 2011). There are also 2 pH-point titration with back titration (DiLallo and Albertson, 1961; Powell and Archer, 1989). Most of these methods verified their applicability by measuring samples of synthetic solutions or effluents from reactors anaerobically treating different types of industrial wastewater (Vannecke et al., 2015). Limited experience has been gained regarding the application of these titration methods on anaerobic digesters treating agricultural resources (Lützhøft et al., 2014; Purser et al., 2014). Naturally, there would be limitation when applying these titration methods in anaerobic digestion of manure which characterized with high solids. The difference between the results from titration methods and lab-instrumental methods for VFA determination in AD processes is still relatively large (Hey et al., 2013; Ibrahim et al., 2014; Lützhøft et al., 2014). This could be attributed to the complex matrix containing high concentrations of interfering components present to a great extent in AD slurry (Kujawski and Steinmetz, 2009; Purser et al., 2014). Moreover, most of the titration procedures studied require sample filtration or centrifugation prior to titration, which increases the equipment costs and complexity of VFA monitoring of AD processes with titration (Lützhøft et al., 2014; Voß et al., 2009). Thus, improving measurement accuracy and simplifying sample preparation are two significant aspects of the VFA monitoring titrimetric technique that need further breakthroughs to achieve on-site practical application. Furthermore, the breakthroughs would ideally be combined with the original titration methods, maintaining their simplicity.

The Nordmann method (Nordmann, 1977)is one of the most common and simple titration methods, and has been widely used in research (Adam et al., 2015; Allen et al., 2014; Browne et al., 2014; Kim and Kafle, 2010; Pagés-Díaz et al., 2015; Rugele et al., 2015; Schwede et al., 2013). The Nordmann method has also been preinstalled in two auto-titrators and an on-line VFA-monitoring machine that are commercially available (Lili et al., 2011; Purser et al., 2014). The Nordmann method has achieved this widespread use because, during one titration process, it uses just two endpoints to gain three outputs: VFA, total inorganic content (TIC), and a ratio value of VFAs to TIC (VFAs/TIC). However, differences between VFAs measured using the Nordmann method and lab-instrument methods have been noted in few studies (Kujawski and Steinmetz, 2009; Purser et al., 2014). Consequently, the Nordmann method could be simpler and more representative when developing a new method, based on the original procedure of Nordmann titration method, as it achieves considerable accuracy with reduced or simplified sample pretreatment.

Therefore, this study undertakes the development and validation of a simplified Nordmann titration method for VFA measurement. The influence of ion interfering and solid interfering subsystems in titrated samples using the Nordmann titration method was first analyzed. The relationship between the different VFAs measured by gas chromatography (GC) and the traditional Nordmann method was then correlated with the content of total solids in the titrated samples. A novel simplified Nordmann method was proposed and validated using a long-term lab-scale anaerobic digestion experiment. These results might assist in the application of the Nordmann titration method in the on-site routine monitoring of biogas plants and the development of low-cost automatic titration devices.

2. Material and methods

2.1. Experiment set up

To develop and validate a simplified Nordmann titration method, the theoretical basis of the original Nordmann method was first analyzed. Then, titrant consumption during the titration process was calculated theoretically to investigate the influence of ion interfering subsystems in the Nordmann method. The influence of solid interfering subsystems was investigated by comparing two continuous titration curves generated from the same sample with and without treatment by centrifugation. To quantitatively describe the relationship between TS content in digested samples and the difference in VFA concentrations measured by the traditional Nordmann method and GC, 22 samples with different TS concentrations were taken from well-operated biogas digesters with various feeding materials of pig manure, chicken manure, and crop straw, were analyzed (detailed information shown in Table 2). A novel simplified Nordmann method was proposed based on in-situ daily gas production (and its composition) and feeding quantity. Finally, this method was validated in a 160-day semi-continuous lab-scale continuous stirred tank reactor (CSTR) experiment of chicken manure fermentation with various organic loading rates of 1–7 g VS $(L{\cdot}d)^{-1}$.

2.2. Nordmann titration method

In 1968, McGhee observed that the acetate system exhibits a quite distinct buffer effect between pH 4 and 5 with very little interfere from the bicarbonate system, and that the slope of the titration curve varies linearly with concentration. Accordingly, he presented a titration procedure for the approximation of VFA concentrations by determining the slope of the titration curve between pH 5 and pH 4 using several test series (McGhee, 1968; Voß et al., 2009). In cases where the titration curve slope begins increasing slightly before pH 4, pH 4.4 was suggested. A linear equation for the slope and concentration was determined, as shown in Eq. (1) (McGhee, 1968).

$$Y = 0.15 + 0.00206 \times X \quad (1)$$

where Y is the reciprocal of the slope (mL/pH unit) and X is the VFA concentration (mg L^{-1} as HAc).

The Nordmann method was developed from McGhee's study which used 0.1 N sulfuric acid solution to titrate cleared samples (20 mL) from their original pH to pH 5 and pH 4.4. However, due to the overlapping buffer zones of bicarbonate and VFAs, it was considered a semi-quantitative determination following empirical investigations of equations deduced from McGhee's linear regression equation (Eq. (1)) (Voß et al., 2009), shown in Eqs. (2)–(4).

$$X = (1.66 \times V_{5-4.4} - 0.15) \times 485.44 \quad (2)$$

$$VFAs \approx (1.66 \times V_{5-4.4} - 0.15) \times 500 \quad (3)$$

$$TIC = V_5 \times 250 \quad (4)$$

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