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# Study on indicators for on-line monitoring and diagnosis of anaerobic digestion process of piggery wastewater



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# HIGHLIGHTS

- The response of state indicators to different types of load disturbances were studied.
- Only H<sub>2</sub>, H<sub>2</sub>S, propionate, TVFAs and biogas yield showed positive response to the load disturbances.
- A combination of H<sub>2</sub>/H<sub>2</sub>S was chosen as the indicators.

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# ABSTRACT

To avoid the instability and failure of anaerobic digestion, a process of monitoring and controlling is strongly required. State indicators including biogas yield, methane content, hydrogen ( $H_2$ ), hydrogen sulphide ( $H_2$ S), pH, total volatile fatty acids (TVFAs) and individual volatile fatty acids were studied under different types of load disturbances in order to find the most effective indicator(s). During load disturbances, biogas yield increased quickly in response to the easily degradable compounds while slowly to the complex compounds. Relatively stable methane content (55.8%–66.0%) and pH (6.6–7.2) were observed.  $H_2$  increased more than 200 times, 6 times and 15 times respectively for glucose, peptone and lipids. While  $H_2$ S increased from 1000 ppm to 3500 ppm, 3500 ppm and 4221 ppm respectively for glucose, peptone and lipid. Not all individual VFAs except propionate made obvious response to the load shocks which rose from 6.5 mmol/L to 49.8 mmol/L, 17.1 mmol/L and 28.1 mmol/L respectively for glucose, peptone and lipids. A combination of  $H_2/H_2$ S was chosen to monitor this kind of digester dealing with piggery wastewater.

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# 1. Introduction

China is a large pig-raising country. There are about 700 million pigs output in 2015, which accounts to over 50% of the world total sum. The number will go up year by year. It means there will be more than 2 billion kg dry pig manure produced every day (calculated by 3 kg per one pig per day). Water flushing excrement cleaning method is the main way to deal with pig manure which brings in a large amount of piggery wastewater. Piggery wastewater is characterized by a high concentration of organic matter, ammonia nitrogen and phosphate. If it is not well treated, it will cause a series of environment problems like water pollutions, water eutrophication and odours. Even though many processes have been developed to treat piggery wastewater, anaerobic digestion has been considered the most feasible process especially in the period of increased costs for non-renewable energy sources (Bocher et al., 2008; Lim and Fox, 2011; Fierro et al., 2014).

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**Table 1**Characteristic of piggery wastewater.

	Value
COD (mg/L)	5200±85
BOD (mg/L)	2700±23
SS (mg/L)	3100±45
TN (mg/L)	850±30
NH <sub>3</sub> -N(mg/L)	720±25
TP (mg/L)	6.8±1.1
рН	6.8±0.4

However, the quantity of wastewater fluctuates greatly mainly because: (1) climate factor. Water consumption in summer is obvious higher than that in winter in order to ensure the safety and health; (2) growth factor. Water consumption will be different among the growth stages of pigs. The variation of quantity in piggery wastewater will cause load disturbances to the bioreactor and may lead instability even failure to the bioreactor. To avoid the instability and failure of anaerobic digestion, a process of monitoring and controlling is strongly required. The ideal sensor should have the following characteristics: (1) indicate an overload timely; (2) do not need much maintenance; (3) not be too expensive considering the application in small plants. The most commonly used state indicators are biogas yield, gas composition, pH, alkalinity and concentration of VFAs (Boe et al., 2010; Gaida et al., 2012; Falk et al., 2015). Biogas yield can indicate the overall process performance and also can be easily measured. However, it cannot indicate process imbalance in time. A decrease in biogas yield often occurred after the process is severely inhibited or already broken down. Since biogas yield is depended on HRT, OLR, and feed composition (Li et al., 2017). pH is relatively straightforward to measure. While it is not a suitable parameter for a well-buffered bioreactor, since the response of pH has low sensitivity in those bioreactors (Nielsen et al., 2007a). Biogas composition is a traditional parameter. Low methane concentration can indicate inadequate process performance (Adam et al., 2015). However, fluctuation of pH can affect the gas composition without decreasing methane production. VFAs are suggested as a control parameter by many researchers since they can indicate the activity of methanogenic bacteria (Molina et al., 2009). Accumulation of TVFAs can be interpreted as either organic over-load or inhibition of the methanogenic microbial communities. While relevance of specific VFAs is still unclear. Except methane and carbon dioxide, biogas also contains small amounts of  $H_2$  and  $H_2S$  (Frare et al., 2010).  $H_2$  is the intermediate product of anaerobic digestion and the intermediate product of propionate and butyrate converted into acetate. It controls the course of substrate utilization which is thought to be an effective parameter for evaluating anaerobic digester performance (Hou et al., 2014). H<sub>2</sub>S is toxic to methane producing bacteria (MPB) (Diaz et al., 2011). Sulphate-reducing bacteria (SRB) may compete with methanogens, acetogens or other bacteria for the utilization of acetate, hydrogen, propionate and butyrate (Damianovic and Foresti, 2007). In this case, the concentration of H<sub>2</sub>S in biogas can be used as a state indicator of anaerobic digestion (Singh and Mandal, 2008; Peu et al., 2012).

Though many works about the indicators have been done by the former researchers, no agreement has been made. Even the indicators have been selected, they may be not suitable for other kinds of reactors or substrates. Some indicators are also complex to test which lead an invalid monitoring to the anaerobic process. Meanwhile, the lack of understanding the relationship between these indicators also results in an inefficiency of indicators.

In order to find the most effective indicator(s), a range of indicators including biogas yield, gas composition, pH, hydrogen concentration, hydrogen sulphide concentration and VFAs are investigated in this study. Meanwhile, the relationships between those indicators are also analysed.

#### 2. Methods and materials

The experiment was carried out in an underground river reactor which was showed in previous study (Cheng et al., 2016). To test the responses of indicators, the experiment was designed as follows: (1) the bioreactor was firstly operated at a stable state in order to get a baseline of those indicators (from day 1–54). Piggery wastewater was used as substrate for the reactor. The characteristic of piggery wastewater was shown in Table 1; (2) load disturbances were introduced by extra organic compounds in order to observe the variation of those indicators and determine the best indicator(s). The extra organic compounds were added into the reactor as follows: glucose added at day 55 was used to represent carbohydrate, peptone added at day 59 was used to represent protein substances, olive oil was used to represent lipid added at day 66; (3)finally an overload of piggery wastewater was fed in at day 74 to test the effectiveness of the indicators which had been determined. Table 2 showed the specific information of the experiment. All the experiments were performed in triplicate biogas reactors with the same operational conditions to eliminate the possible error.

During the operation, response of indicators was monitored. The available online measurement indicators included biogas yield, pH and hydrogen concentration. Off-line indicators included biogas composition, hydrogen sulphide concentration, TVFAs and individual volatile fatty acids. Biogas composition was determined with a gas chromatograph equipped with a thermal conductivity detector (TCD) and 5A molecular sieve column. The injector, detector and oven temperatures were 80 °C,150 °C and 180 °C, respectively. Argon was served as the carrier gas. TVFAs was measured according colorimetric method. Individual VFA concentrations were measured by a gas chromatograph equipped with a flame ionization detector

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