Biogas-pH automation control strategy for optimizing organic loading rate of anaerobic membrane bioreactor treating high COD wastewater

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HIGHLIGHTS

- Novel control strategy doubled OLR of AnMBR treating high COD wastewater.
- COD removal rate achieved 99.1% allow for efficient and compacted digestion.
- Gas-liquor two phase monitoring sensitively reflected digestion status.
- Dynamic kinetic and pH titration determined exact threshold for control object.
- The novel strategy seized CO₂ for ternary buffer system and maintained pH > 7.4.

GRAPHICAL ABSTRACT

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ABSTRACT

Control of organic loading rate (OLR) is essential for anaerobic digestion treating high COD wastewater, which would cause operation failure by overload or less efficiency by underload. A novel biogas-pH automation control strategy using the combined gas-liquor phase monitoring was developed for an anaerobic membrane bioreactor (AnMBR) treating high COD (27.53 g·L⁻¹) starch wastewater. The biogas-pH strategy was proceeded with threshold between biogas production rate >98 Nml·h⁻¹ preventing overload and pH > 7.4 preventing underload, which were determined by methane production kinetics and pH titration of methanogenesis slurry, respectively. The OLR and the effluent COD were doubled as 11.81 kgCOD·kgVSS⁻¹·d⁻¹ and halved as 253.4 mg·L⁻¹, respectively, comparing with a constant OLR control strategy. Meanwhile COD removal rate, biogas yield and methane concentration were synchronously improved to 99.1%, 312 Nml·gCOD_{in}⁻¹ and 74%, respectively. Using the biogas-pH strategy, AnMBR formed a “pH self-regulation ternary buffer system” which seizes carbon dioxide and hence provides sufficient buffering capacity.

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1. Introduction

Owing to huge discharged quantity of chemical oxygen demand (COD) (e.g., 4.7 × 10⁶ ton in 2013) and its threat to aquatic environment, the food processing wastewater was targeted in the 10 most polluting industrial wastewaters by the Action Plan for Water Pollution Prevention and Control of China issued recently (Chinese State Council, 2015). Due to high COD removal performance,

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anaerobic membrane bioreactor (AnMBR) could provide a promising way for food processing wastewater treatment to achieve the stringent COD discharging standard ($\text{COD} < 500 \text{ mg} \cdot \text{L}^{-1}$) of GB 8978-1996 without further polishing (Wei et al., 2014). But the organic loading rate (OLR) of the AnMBR at $2.1\text{--}8.6 \text{ kgCOD} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$ is relatively low in food processing wastewater treatment by AnMBR, caused by unpredictable constituents of food processing wastewater and limited biomass concentration of AnMBR (Liao et al., 2006; Lin et al., 2012). The unpredictable constituents were related to various food products, seasonal changes of post harvesting and food processing, leading to unstable COD and pH of wastewater (Lin et al., 2012). With limited biomass, one of the critical challenges of treating high COD wastewater by AnMBR is how to maximize OLR, which would cause high effluent COD concentration and unstable operation by overload (Tay and Zhang, 2000), or less efficient performance by underload (Menardo et al., 2011). Overload of the anaerobic digestion (AD) implies a risk of process upset, and is usually interpreted as the result of methanogenesis inhibition (Pind et al., 2003). Another drawback of overload is inhibition on methanation process, resulting in 30% losses of potential methane production yield (Fotidis et al., 2014). Methane production losses would not only limit the energy recovery and reduce COD removal rate, but also bring about more expensive downstream treatment, and these will obviously prevent widespread application of the AnMBR in food processing wastewater treatment. There is therefore considerable impetus to optimize OLR of AnMBR treating high COD food processing wastewater.

The online monitoring and automation control strategy provides a new way for real-time optimizing OLR of AnMBR for unpredictable food processing wastewater, and usually consists of online monitoring parameters and automation control strategy. Proper monitoring parameters which could reflect AnMBR state and feed constituents in an accuracy, stability and easy maintenance way, still remain great difficulties due to the complexity of sample pretreatment and huge fluctuations of sample characteristics (Boe et al., 2010). The combined monitoring of both liquid and gas-phase parameters is thus considered as an efficient way for the anaerobic digestion (AD) process (Madsen et al., 2011). Lots of methods have been developed for online monitoring of parameters in both the liquid and gas phases of AD, including chromatography (Lenz et al., 2011; Ward et al., 2011), pH titration (Lutzhof et al., 2014), fuel cell (Liu et al., 2011), and spectroscopy (Ward et al., 2011), but their applications are limited in practice owing to robustness and accuracy. For example, gas chromatography is the most accurate method for volatile fatty acids (VFAs) monitoring in liquid phase, but pretreatment of liquid samples is great challenge due to complexity of AD slurry (Lenz et al., 2011; Ward et al., 2011). Titration could be directly applied in monitoring total VFAs of the AD slurry, but its accuracy is limited by variation of pH buffer capacity (Lutzhof et al., 2014). Due to these obstacles of VFA online monitoring, pH titration of offline samples was more widely applied than online monitoring in biogas plants (Lutzhof et al., 2014). The most widely used and accurate online monitor parameters of the liquid-phase are pH and oxidation–reduction potential (ORP) based on electrochemical method which are sensitive and maintenance friendly (Madsen et al., 2011). Furthermore, combination of pH and ORP also reflects fermentation pathway which links to methanogenesis efficiency (Ren et al., 2002). Spectroscopy has more application in monitoring parameters of gas phase than liquid phase, i.e., near-infrared (NIR) for gas components (Ward et al., 2011), but is limited by sensitivity in biogas monitoring. Recent progress in accuracy of biogas flow rate monitoring made it very attractive approach for gas-phase online monitoring. Monitoring pH of the liquid-phase and biogas flow rate of the gas-phase could work as robust parameters for AnMBR treating high COD food processing wastewater.

The automation control strategy for wastewater treatment by anaerobic digestion is more experiential based on black-box model, such as threshold (Boe et al., 2010), difference index (Dong et al., 2011) and fuzzy logic (Pind et al., 2003), rather than knowledge based on dynamic model remains immaturity (Pind et al., 2003). Based on the combined gas–liquid phase monitoring, many experiential control strategies were thus developed concisely and stably (Dong et al., 2011; Liu et al., 2014; Madsen et al., 2011). The combined gas–liquid phase monitoring makes it possible to indicate digester state by simple parameters, rather than complex parameters in the liquid only. For example, an online monitoring and alert system based on different index of methane production rate and total VFA concentration was developed for a UASB treating sucrose-rich synthetic wastewater ($\text{COD} 5000 \text{ mg} \cdot \text{L}^{-1}$) (Dong et al., 2011), resulting in as high as OLR of $10 \text{ kgCOD} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$ and as low as effluent COD concentration of $224 \text{ mg} \cdot \text{L}^{-1}$. A novel online diagnose system combining microbial fuel cell (MFC), gas flow meter and pH meter was developed for a upflow anaerobic fixed bed reactor (UAFBR) treating starch wastewater (Liu et al., 2011, 2014), reached OLR of $3.45 \text{ kgCOD} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$ and effluent COD $1000 \text{ mg} \cdot \text{L}^{-1}$, respectively. Although these complex monitoring strategies were attractive and potential, process analytical technologies (PAT) still need more investigations and progresses in instrument and insight of AD models (Madsen et al., 2011). In these works, the most commonly used parameters are still pH, VFA and biogas flow rate, which are well related but sensitive in different situations. For potato processing starch wastewater which was of low alkalinity and pH, pH was a sensitive alert of overload which leads to VFA accumulation and methanogenesis inhibition (Colin et al., 2007; Liu et al., 2014). On the contrary, underload of methanogenesis can be monitored by biogas production rate (Liu et al., 2014; Stromberg et al., 2015). In a summary, the combined monitoring of biogas flow rate in the gas phase and pH in the liquid phase may provide sensitive thresholds based digestion dynamic. Therefore, the dynamic thresholds could be used for OLR control strategy based on dynamic model in the AnMBR treating high COD food processing wastewater.

Therefore the aims of this study was to develop a new biogas–pH automation control strategy for optimizing organic loading rate (OLR) of AnMBR treating high COD food processing wastewater, in which the combined biogas–pH monitoring and controlling thresholds were determined by methane production kinetics and pH titration of methanogenesis slurry, respectively. Meanwhile the formation mechanism of pH self-regulation ternary buffer system was investigated in the AnMBR operated with this control strategy.

2. Methods

2.1. Schemes of AnMBR and its online monitoring & control system

A bench-scale AnMBR used in this work consisted of an acidogenesis reactor of 2.0 L (working volume) and a methanogenesis reactor of 4.0 L (working volume), respectively. The online monitoring and automation control system consisted of a gas-phase detection unit and a liquid-phase detection unit that connected to a computer through serial ports (RS232/485, Siemens AG, Germany) of programmable logic controller (PLC, SIMATIC S7-200 CPU224XP, Siemens AG, Germany), as illustrated in Fig. 1. The liquid-phase online monitoring unit was a pH sensor (E201-C, Leici Instrument Incorporated, Shanghai, China) for monitoring pH drop in the methanogenesis reactor due to feed overload. The gas-phase online monitoring unit was a gas flow meter (μFlow , Bioprocess Control AB, Sweden) for monitoring decreases of biogas production rates in the methanogenesis reactor due to feed underload.

Fig. 1. Schematic diagram of a lab-scale two-phase anaerobic tubular membrane bioreactor.

The software of this automation control system was designed on the basis of an industrial control configuration software (MCGS, Kunluntongtai Co., China), incorporating multi-function of data acquisition, recording and display, especially equipment automation control. The monitoring data were collected by the PLC, and then real-time recorded and proceeded by the software. The feed pump (BT100, Longer Co., China) of starch wastewater was automatically controlled by the software.

2.2. Dynamic threshold determination for the biogas-pH strategy

The dynamic threshold of the biogas production rate in the methanogenesis reactor for prevention overload was determined by methane production rates in biochemical methane potential (BMP) test of methanogenesis phase (Ince et al., 1995) according to OLR of the methanogenesis reactor of the AnMBR. The BMP tests for determining methane production rates were carried out in four parallel using a commercial laboratory instrument (AMPTS II, Bio-process Control, Sweden) which contains 15 parallel cells. Each cell consists of three parts including mesophilic reactor with total volume of 500 ml, CO_2 absorption by NaOH solution (3 M), and gas meter with a data acquisition system (Sambusiti et al., 2014). To simulate methane production rates in the methanogenesis reactor of the AnMBR, an amount of 50 ml effluent of the acidogenesis reactor (as substrates, $\text{COD } 23.21 \pm 0.46 \text{ g}\cdot\text{L}^{-1}$, $\text{VS } 6.68 \pm 0.17 \text{ g}\cdot\text{L}^{-1}$) was mixed with 150 ml slurry of the methanogenesis reactor (as inoculums, $\text{COD } 1.66 \pm 0.03 \text{ g}\cdot\text{L}^{-1}$, $\text{VS } 10.01 \pm 0.21 \text{ g}\cdot\text{L}^{-1}$) at OLR of $5.81 \pm 0.11 \text{ kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$, which total work volume was one twentieth of the methanogenesis reactor. The methane production rates of the BMP test were then converted to the biogas production rate in the methanogenesis reactor through divided by 65% (aver-

age methane concentration in biogas), and then multiplied by 20 ($V_{\text{Methanogenesis}}/V_{\text{BMP}}$).

The threshold of pH in the methanogenesis reactor for prevention overload was selected according to pH variation in titration of slurry in the methanogenesis reactor, which thresholds were pH 6.5–8.2 and VFA 1000–1500 $\text{mg}\cdot\text{L}^{-1}$ for the optimized biogas and methane production (Mao et al., 2015). To minimize risks of VFA accumulation and OLR underload, the optimized VFA concentration was selected as 1000 $\text{mg}\cdot\text{L}^{-1}$. The slurry samples (100 ml) were titrated with 10 $\text{g}\cdot\text{L}^{-1}$ acetic acid solution 1 ml once a time, so that acetic acid concentration in the slurry was increased with step of 100 $\text{mg}\cdot\text{L}^{-1}$, and after mixed the stable pH was measured and recorded (Liu et al., 2014). Other VFAs were also performed exactly the same including propionic, *n*-butyric, *iso*-butyric, and *n*-valeric acids, respectively.

2.3. Biogas-pH automation control strategy

The biogas-pH automation control strategy is shown in Fig. 2. The biogas flow rate in the gas-phase and pH in the liquid-phase were measured online by the sensors and transported to the PLC, and all detections were conducted once per minute. When the biogas production rate in the methanogenesis reactor was under $98 \text{ NmL}\cdot\text{h}^{-1}$, the feedstock was pumped until pH under 7.4 in the methanogenesis reactor. The threshold data of biogas and pH were determined by the BMP tests and pH titration of methanogenesis according to the purposes which were discussed in Section 3.3. Specifically, if a change of sign occurs, the system will not give an immediate judgment. Instead, it would evaluate whether such a signal change is caused by a real change of reactor status or just a temporary fluctuation according to the average of last a quarter and the subsequent points in at least 30 min (Dong et al., 2011).

Fig. 2. Flow chart of the biogas-pH automation control strategy for optimizing OLR of the AnMBR.

The automatic control strategy for optimizing OLR of the AnMBR was continuously operated for 18 weeks (day 70–196).

2.4. Operations of AnMBR

The seed sludge for the AnMBR was taken from an egg-shaped digester of Xiaohongmen Wastewater Treatment Plant, Beijing, China. The pH of the seed sludge was 7.31 ± 0.03 . High COD starch wastewater was used as feedstock, which was characterized at COD of $27.61 \pm 3.49 \text{ g}\cdot\text{L}^{-1}$ and SS of $6.21 \pm 0.84 \text{ g}\cdot\text{L}^{-1}$, respectively, as listed in Table 1. Temperatures in the two reactors of the AnMBR were maintained $37 \pm 0.3^\circ\text{C}$ by water bath. The AnMBR was firstly started at a fixed OLR of $5.88 \pm 0.63 \text{ kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ according to literature (Fang et al., 2011) before the biogas-pH control strategy was applied. As far as the high rate AD treating high COD food processing wastewater is concerned, the two-phase anaerobic digestion is usually applied for mitigating acidification risk and the methanogenesis is the speed-limited step (Wei et al., 2014). Therefore the OLR in this study refers to the methanogenesis phase of the AnMBR. The raw wastewater was screened (0.1 mm) before entering the AnMBR to protect membrane.

Operation of the AnMBR was divided as two stages: (1) constant OLR control strategy stage (Stage-I, day 0–70) as the control group; (2) biogas-pH control strategy stage (Stage-II, day 70–200) as the experiment. In the Stage I, the feedstock of the AnMBR was automatically pumped at 30 s every 10 min by the PLC. Temperature, mixing, and water level were maintained by the daemon process in the PLC. ORP was used as alert for abnormal status of methanogenesis reactor which was rarely activated in this work. The methanogenesis reactor reached a steady state in terms of OLR at $5.70 \pm 0.49 \text{ kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ and effluent COD at $445.17 \pm 135.59 \text{ mg}\cdot\text{L}^{-1}$ in day 63–84, but the effluent COD concentration cannot meet the indirect discharge standard (COD < $500 \text{ mg}\cdot\text{L}^{-1}$) of GB 8978-1996. After the AnMBR was initialized with the constant OLR control strategy, the biogas-pH automation control strategy was loaded in the PLC and conducted to maximize OLR in order to make the effluent COD concentration meet requirements of the abovementioned indirect discharge standard.

2.5. Analysis

Samples were taken from the two reactors of the AnMBR twice a week. Chemical oxygen demand (COD) was measured using a

DR2500 (HACH Inc., USA) according to Chinese standard methods (GB11914-1989). Total carbon (TC), total organic carbon (TOC) and total inorganic carbon (TIC) were determined with a liquiTOC II (Elementar Analysensysteme GmbH, Germany) (Wang et al., 2015). Ammonia ($\text{NH}_4^+\text{-N}$), nitrite (NO_2^-), nitrate (NO_3^-), total nitrogen (TN), and $\text{PO}_4^{3-}\text{-P}$ were measured using a SmartChem200 (Alliance Inc., France), and each of their values in Fig. S1 was the average of duplicate samples during the two stages. The soluble COD was measured with the filtrate samples through a $0.22 \mu\text{m}$ membrane. The concentrations of total suspended solids (TS) and volatile suspended solids were determined at 104°C (4 h) and 600°C (2 h), respectively. CH_4 and CO_2 concentrations in the biogas were determined by a gas chromatography (GC, 4890D, Agilent Inc., USA) equipped with 6-way valve gas sampler, 2 m column packed with 13XMS (60/80 mesh) and flame ionization detector (detecting details listed in Supporting Information).

3. Results and discussion

3.1. Performance of the biogas-pH strategy

The OLR, COD concentration of influent and effluent, and COD removal rate of the AnMBR were shown in Fig. 3 and Table 1. Stage-I was used as the blank group for determining OLR changes and their effects on the AnMBR performance. The initial OLR of the AnMBR in Stage-I was set at $5.28 \text{ kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ according to reported OLR of $5.1 \text{ kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ of potato starch wastewater (Fang et al., 2011). The effluent COD concentration and COD removal rate were $698 \text{ mg}\cdot\text{L}^{-1}$ and 97.3%, respectively. Considering AnMBR has a high OLR for biomass retention, the OLR of the AnMBR during day10–36 was gradually increased to $8.05 \pm 0.90 \text{ kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$, but the effluent COD concentration increased to $752.80 \pm 263.35 \text{ mg}\cdot\text{L}^{-1}$ and the COD removal rate dropped to $97.17 \pm 0.99\%$, in accordance with other two-phase anaerobic digestion (Rincon et al., 2008). Correspondingly, the pH in the methanogenesis reactor dropped under 7.4–7.5, which was in accordance with the results while OLR increased to $6.4 \text{ kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ (Fang et al., 2011). Due to the fluctuant effluent COD concentration failed to meet the Chinese discharge standard of COD < $500 \text{ mg}\cdot\text{L}^{-1}$ (GB 8978-1996), the OLR was then gradually decreased back to the initial OLR of $5.66 \pm 0.50 \text{ kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ during day 36–58. This operation resulted in decrease of effluent COD concentration to $402.12 \pm 148.70 \text{ mg}\cdot\text{L}^{-1}$ which could meet

Fig. 3. Effects of the biogas-pH automatic control strategy on OLR and sCOD.

the Chinese discharging standard (GB 8978-1996), and steeply increase of COD removal rate to $98.47 \pm 0.65\%$ during day 58–70. From Stage-I results, it was concluded that the OLR of $8.05 \pm 0.90 \text{ kgCOD} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$ was too high for the AnMBR operated with the constant OLR operating strategy.

For optimizing the OLR, the biogas-pH automation control strategy was launched in Stage-II. Results demonstrated that a 52.9% improvement in the OLR, $8.66 \pm 0.25 \text{ kgCOD} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$ during day 84–98, occurred after two weeks of this strategy started, compared to that in Stage-I. Meanwhile, effluent COD concentration was decreased to $358 \pm 78.24 \text{ mg} \cdot \text{L}^{-1}$, much lower than COD $500 \text{ mg} \cdot \text{L}^{-1}$ of the Chinese discharge standard (GB 8978-1996). The effluent COD concentration remained lower than $300 \text{ mg} \cdot \text{L}^{-1}$, though the OLR of the AnMBR gradually climb up to $10.45 \pm 1.42 \text{ kgCOD} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$ in day 98–161. These improvements led to the final steady-state (day 161–194) with the OLR of $11.81 \pm 0.31 \text{ kgCOD} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$ operating continuously for more than 28 days, 208.7% higher OLR than that in the steady state of Stage-I (day 36–58). Additionally, effluent COD concentration and COD removal rate were synchronously decreased to $253.4 \pm 43.70 \text{ mg} \cdot \text{L}^{-1}$ and improved to $99.1 \pm 0.20\%$, respectively. These results showed that the biogas-pH automation control strategy not only enhanced stability in high OLR operation of the AnMBR, but also improved performance in COD removal and effluent COD concentration (Table 1) of the AnMBR.

The average biogas yield was increased from $275 \pm 61 \text{ Nml} \cdot \text{gCOD}_{\text{in}}^{-1}$ (Stage-I) to $312 \pm 49 \text{ mL} \cdot \text{gCOD}_{\text{in}}^{-1}$ with the biogas-pH control strategy (Table 1). One important reason for the improvement could be attributed to more influent COD was removed. The average biogas flow rate was doubled as $596 \pm 327 \text{ Nml} \cdot \text{h}^{-1}$ compared with the constant strategy, owing to the doubled organic loading rate. And the peak biogas production rate ($647.79 \pm 177.96 \text{ mL} \cdot \text{h}^{-1}$) in the stable period of Stage-II was also 38% higher than that ($401.30 \pm 115.36 \text{ mL} \cdot \text{h}^{-1}$) in the initial period of Stage-II. But the methane concentration did not share the similar increasing trends with biogas flow rate (Fig. 3). It was very stable at the volume concentration of $70.5 \pm 0.6\%$ in the optimizing period of Stage-I, so did the pH. The methane concentration was decreased with the initiating of the new strategy which might

link with insufficient substrate and needs further research (Ahiring, 2003). But it recovered to $74.1 \pm 6.3\%$ during the optimizing and stable periods of Stage-II. And then methane concentration reached several peak points over 80% which might be attributed to that the higher pH seizing more carbon dioxide at the end of every control cycle.

The largest obstacle of COD removal is providing sufficient carbonate alkalinity when treating starch wastewater in high rate AD (Ahiring, 2003). In order to provide sufficient carbonate alkalinity, many investigations have been carried out, in the effort to reduce the cost necessary to balance the pH in reactor. For example, one approach was to supply extra alkalinity by bicarbonate to 2000–3000 $\text{mg} \cdot \text{L}^{-1}$ and maintained pH 7.0–7.5 only in the start-up period, which 77.5–92.0% of COD were removed at OLR 10.2–40.0 $\text{kgCOD} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$ in an up-flow multi-stage anaerobic reactor (UMAR) (Sun et al., 2012). But the addition of chemicals is the largest operational cost in all high-rate AD system (Romli et al., 1994). Another approach is to make full use of by-production CO_2 through recirculation of effluent or biogas, which will be more efficient if coupled with upflow anaerobic sludge blanket (UASB) or Internal Circulation (IC) reactor. The accomplished recirculation ratio, COD removal rate and OLR of an UASB treating starch wastewater were 4, >95% and 10–16 $\text{kgCOD} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$, respectively (Annachhatre and Amatya, 2000). The approach is to make full use of CO_2 through the biogas-pH automation control strategy, and to couple with a two-phase anaerobic digestion and membrane separation, details are discussed in the following Section 3.4. The accomplished COD removal rate and OLR in this study were as high as 99.1% and $11.81 \pm 0.31 \text{ kgCOD} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$, respectively. Additionally, a side-effect of higher pH in the methanogenesis reactor is of course retaining of CO_2 , resulting in higher methane concentration in the biogas.

3.2. Procedures of the biogas-pH strategy

The online monitoring records of biogas production rate, pH, cumulative influent mass, and ORP were shown in Fig. 4a. Biogas production rate and pH followed different patterns in Stage-I and Stage-II. In the constant OLR control stage (Stage-I, day 0–70),

Table 1

Feed starch wastewater characteristics, reactor configurations, and operation conditions of AnMBR at different control strategies.

Feed Starch wastewater (average ± SD)					
COD (g.L ⁻¹)	27.53 ± 4.04	Total Solid (g.L ⁻¹)		9.21 ± 1.06	
NH ₄ -N (mg.L ⁻¹)	518.57 ± 232.96	Volatile solids (g.L ⁻¹)		6.17 ± 8.57	
NO ₃ ⁺ -N (mg.L ⁻¹)	12.81 ± 6.83	pH		4.86 ± 0.85	
TN (mg.L ⁻¹)	559.77 ± 23.7	ORP (mV)		27.06 ± 113.66	
PO ₄ ³⁻ -P (mg.L ⁻¹)	281.37 ± 20.41	Electrical conductivity (mS.cm ⁻¹)		7.10 ± 0.71	
TOC (mg.L ⁻¹)	7531.00 ± 1678.2	TIC (mg.L ⁻¹)		389.05 ± 313.78	
Configurations					
Volume of bioreactor (L)	6 L				
Type of acidogenesis reactor	Anaerobic baffled reactor with 2 L working volume				
Type of methanogenesis reactor	Continuous stirred-tank reactor with 4 L working volume				
Recycling pump	Model: FUJ-370A, Q = 35 L/min, P = 120 kPa, 220 V 370 W				
Membrane module	Tuber, PVDF, pore size 0.1 µm, membrane area 0.125 m ²				
Operational conditions					
Control strategy	Stage-I/II	Constant OLR (Stage-I)		Biogas-pH (Stage-II)	
	Initial	Optimizing	Stable	Optimizing	Stable
Time (day)	1–14/70–84	14–58	58–84	84–161	161–194
Organic loading rate (kg _{COD} .kg _{VSS} ⁻¹ .d ⁻¹)	5.28	8.05 ± 0.90	5.66 ± 0.50	8.66 ± 0.25	11.81 ± 0.31
COD Removal Rate (%)	97.3	97.17 ± 0.99	98.47 ± 0.65	98.70 ± 0.28	99.1 ± 0.20
Effluent COD (mg.L ⁻¹)	698	752.8 ± 263.3	402.1 ± 148.7	358 ± 78.24	253.4 ± 43.70
pH (Methanogenesis)	7.82 ± 0.03	7.55 ± 0.12	7.27 ± 0.05	7.60 ± 0.27	7.83 ± 0.29
TIC (mg.L ⁻¹)	364 ± 29	548 ± 127	685 ± 91	672 ± 161	706 ± 48
NH ₄ ⁺ -N (mg.L ⁻¹)	532 ± 13	591 ± 84	827 ± 149	822 ± 84	1086 ± 206
Biogas flow rate (Nml.h ⁻¹)	255 ± 92	404 ± 166	291 ± 106	429 ± 239	596 ± 327
Biogas yield (Nml.gCOD _{in} ⁻¹)	218 ± 80	264 ± 76	275 ± 61	271 ± 96	312 ± 49
Methane Concentrate (%)	69.7 ± 1.5	70.5 ± 0.6	67.3 ± 5.2	69.4 ± 3.9	74.1 ± 6.3
SRT (days)	~200 d				

starch wastewater was fed with a constant rate, and thus biogas production and pH randomly fluctuated around an average value which was 483.4 ± 444.6 ml·h⁻¹ and 7.39 ± 0.01 , respectively. The pH data was similar to that of anaerobic digestion fed with potato juice wastewater (Fang et al., 2011). But the biogas production rate was fluctuant in this work rather than inhibited in the literature report (Fang et al., 2011). After the biogas-pH strategy was applied in Stage-II, the wastewater feeding was started by biogas production rate and stopped by pH. After biogas production rate <98 ml·h⁻¹, the wastewater feeding (with pH = 4.62 ± 0.21) was started meanwhile pH began to decrease. When pH was dropped <7.4, the wastewater feeding was stopped and then biogas production rate recovered immediately.

In stage-II, the pattern of pH and ORP changes indicated underload and overload of methanogenesis reactor. After the biogas-pH control strategy applied, the biogas production rate gradually decreased from 483.4 ± 444.6 ml·h⁻¹ to none and the pH began to increase from 7.39 to over 8.1, which indicated temporary underload of the methanogenesis phase (Liu et al., 2014). When the biogas production rate was less than 98 ml·h⁻¹ for 30mins, the methanogenesis reactor was fed for preventing underload. The fed was lasted to pH under 7.40 for precaution of overload (Fang et al., 2011). The ORP of methanogenesis phase was stable around -263.0 ± 6.5 mV in both Stage-I and Stage-II (Fig. 4a). The ORP and the pH of acidogenic reactor were -126.3 ± 19.5 mV and 4.62 ± 0.21 , respectively, which were tested by a Multi 3210 (WTW GmbH, Germany) twice a week. The dynamic threshold of both biogas and pH were determined according to kinetic study results of the methanogenesis phase, which was discussed in the next Section 3.3.

During the initial period of Stage-II, the pH increased from 7.39 ± 0.01 to 8.11 ± 0.01 and continually increased to 8.12 ± 0.02 in the next cycle. This pH increase relieved the overload of the methanogenesis reactor, and led to an average of 53% more stable biogas production in the Stage-II (470.97 ± 208.40 ml·h⁻¹) compared to that in the Stage-I (483.37 ± 444.63 ml·h⁻¹).

Manipulation of pH variation in the biogas-pH automation control strategy could provide more beneficial conditions to the

methanogenesis reactor than the constant OLR strategy, and ultimately led to more stable operation and better performance of the AnMBR, such as higher OLR, higher COD removal rate, lower effluent COD concentration and higher methane production. These beneficial conditions might be less VFA accumulation and periodically relieved ammonia inhibition owe to higher pH and its periodically increasement. While the OLR was attempted increasing to 6.4 kgCOD·m⁻³·d⁻¹ in a typical constant OLR control strategy in this study, the pH in the methanogenesis reactor was around 7.4–7.5, corresponding to VFAs concentration accumulated to 1000 mg·L⁻¹ (Saddoud and Sayadi, 2007), and hence resulting in average effluent COD 995.17 ± 350.59 mg·L⁻¹, which failed to fulfill the effluent COD constraint during day 29–47. During a typical biogas-pH strategy controlled cycle, the pH in the methanogenesis reactor was decreased to 7.4–7.5 when substrate was just fed and gradually increased to 8.1 at the end of the cycle. What makes the biogas-pH automation control strategy attractive is that inhibition caused by VFAs accumulation and underload of OLR were all minimized by the temporal manipulated pH variations. Meanwhile, ammonia inhibition was temporary relieved by the periodically pH drop of the biogas-pH strategy. In the beginning of the cycle controlled by the biogas-pH strategy, ammonia inhibition was the critical limiting factor (Fotidis et al., 2014) as sufficient substrates were provided. According to the average ammonia concentration of 780.27 ± 250.87 mg·L⁻¹ in the methanogenesis reactor, free ammonia nitrogen (FAN) decreased from 132.84 ± 42.71 mg·L⁻¹ to 29.86 ± 9.60 mg·L⁻¹ when the pH in the methanogenesis reactor decreased from 8.1 to 7.4. The 102.9% decrease of FAN relieved the ammonia inhibition greatly, and hence accelerated the acclimation for periodically relieving FAN inhibition (Fotidis et al., 2014). And the methanogenesis activities increased in the temporal high OLR period at beginning of the cycle thanks to the acclimation (Nielsen and Angelidaki, 2008). At the end of the cycle with substrates eliminated, when substrate was digested and pH increased to 8.1, sufficient bicarbonate acid (BA) was more retained for the next cycle. As sufficient BA was retained, the following cycle could benefit from the endogenous BA supplies, and greatly decrease the cost of addition chemicals such as NaOH

Fig. 4. Procedure and dynamic threshold determination of the biogas-pH control strategy: (a) procedure, (b) methane production rate, (c) pH variation of five kinds VFA added, respectively.

which is the largest operation cost of the high-rate AD systems treating carbohydrate-base wastewaters (Romli et al., 1994).

3.3. Dynamic threshold determination of the biogas-pH strategy

Methane production dynamics in BMP tests of the methanogenesis reactor were reported in Fig. 4b. The methane production rate can be divided into typical three periods of Michaelis–Menten model (Stromberg et al., 2015), including zero order reaction at the 1st period and first order reaction in the 2nd period and low-speed reaction in the 3rd period. The methane production rate achieved in the 1st period was the highest at 16.23 ± 3.51 Nml·h⁻¹ as sufficient substrates were supplied, corresponding to biogas production rate 479.78 ± 104.20 Nml·h⁻¹ in the methanogenesis reactor of the AnMBR. The methane production rate decreased rapidly to around 3 Nml·h⁻¹ in the 2nd period as substrates concentrates decreasing, which the average methane production rate was 3.28 ± 2.49 Nml·h⁻¹ corresponding to the biogas production rate 98 ± 74 Nml·h⁻¹ in the methanogenesis reactor of the AnMBR. The methane production rate gradually decreased to around 1 Nml·h⁻¹ in the 3rd period. To decrease the effluent COD concen-

tration, the average biogas production rate of 98 Nml·h⁻¹ in the end of 2nd period was selected as the underload dynamic threshold, because the substrates concentration is the determining factor in the two periods. Aiming to maximize the OLR, the average biogas production rate 479.78 Nml·h⁻¹ of the 1st period was selected as the underload dynamic threshold. Meanwhile, these two periods were accomplished in 60 hours associate with the HRT 56.5 h of final Stage-II.

Variation of pH during titration of slurry in the methanogenesis reactor is shown in Fig. 4c, different VFAs showed similar pH decreasing trends with VFAs dosage increasing. When the dosed acetic acid concentration increased from 100 mg·L⁻¹ to 2000 mg·L⁻¹, pH of methanogenesis slurry was decreased from 8.13 to 6.65, and other VFAs had similar trends to acetic acid. To prevent the methanogenesis reactor of the AnMBR from overload, the overload dynamic threshold was selected as VFA 1000 mg·L⁻¹ corresponding pH ranged from 7.24 to 7.42 (Mao et al., 2015). To minimize the overload risk, the overload threshold was selected at pH 7.4 in this study. What is more, the threshold can be reset according to the kinetic studies for different optimizing objectives. For example, lower biogas dynamic threshold can be selected for

Fig. 5. Mechanism of pH self-buffer capacity of the AnMBR in Stage-II.

higher OLR without the effluent COD constraint, and higher pH threshold can be selected to minimize the risks of VFAs accumulation.

3.4. Mechanism of the biogas-pH strategy

To demonstrate how the pH variations was dominated by a ternary buffer system composed by VFAs, ammonia and carbonate, a ternary contour was carried out to visualize the pH variations in the ternary buffer system (Fig. 5). Since truly simulating the pH variation in the methanogenesis reactor of the AnMBR is exceedingly difficult due to big amounts of electrolytes, the ternary macro-quantity buffer salts were selected for the visualization which represents the critical pH buffer capacity of the methanogenesis (Mao et al., 2015). The pH of buffer system is dominated by weak acids and mild base salts as Eq. (1). Results of the methanogenesis reactor of the AnMBR showed that concentrations of TIC, TOC and ammonia nitrogen were $915.00 \pm 265.23 \text{ mg}\cdot\text{L}^{-1}$, $629.32 \pm 273.21 \text{ mg}\cdot\text{L}^{-1}$ and $780.27 \pm 250.87 \text{ mg}\cdot\text{L}^{-1}$, respectively (Fig. A.1 and A.2). So the ternary contour ranges of carbonate acid, acetic acid and ammonia were set at $0\text{--}3000 \text{ mg}\cdot\text{L}^{-1}$, $0\text{--}1500 \text{ mg}\cdot\text{L}^{-1}$ and $0\text{--}1500 \text{ mg}\cdot\text{L}^{-1}$, respectively, which were extended to double value of their practical concentrations in the methanogenesis reactor of the AnMBR. The accordance of ternary contour (Fig. 5b) and pH titration (Fig. 4c) verified the assumption that the variation of pH largely dominated by the ternary buffer system. Variation ranges of pH were 3.8–10.86 (CO_3^{2-}), 8.96–3.51 (acetic acid) and 9.49–6.6 (ammonia), respectively, which were more affected by CO_3^{2-} than by acetic acid and NH_4^+ among the test ranges. In addition, there is a pH basin (~ 6.42) around $1200 \text{ mg CO}_3^{2-}\cdot\text{L}^{-1}$ which is caused by bicarbonate acid (NH_4HCO_3).

This is the first time that the pH self-buffer system was discussed in AnMBR, which had such a profound improvement in pH control without adding extra chemicals. Such pH ternary self-buffer system produced by the biogas-pH automation control strategy would provide a new approach to solve the acidification problem in AnMBR and the high-rate AD systems compared to the current methods used today.

Provided that online manipulating concentration of ternary buffer system is available, this manipulated variable becomes superior to pH manipulation in the reactor when the control objective is sufficient alkalinity for AD system. In addition, by spatially separating anaerobic digestion into two reactors, the acidification reactor was enriched with VFAs and the methanogenesis reactor was enriched with ammonium-bicarbonate buffer solution (Rincon

et al., 2008). By temporally fed control, the pH in the methanogenesis reactor can be regulated via VFA dosages or ratio between VFAs and NH_4HCO_3 (Zhang et al., 2015). By periodically decreasing the VFAs concentrations, the biogas-pH strategy would enhance the retention of bicarbonate acid which provides more stable pH and sufficient alkalinity for the AD system. Thus the pH in the methanogenesis reactor can be self-regulated by manipulating spatio-temporal distribution of carbonic acid, VFAs and ammonia using the two-phase AD and the fed controlled by the biogas-pH strategy without any extra addition only, which is named as the “self-regulation pH buffer system” in this study.

Another merit of the biogas-pH automation control strategy in this study is acclimatization of ammonia by periodically relieving free ammonia nitrogen (FAN) inhibition. Ammonia is one of the most common inhibitors in anaerobic digestion of food processing wastewater, e.g., starch wastewater or potato juice wastewater. For example, with a low ammonia concentration around $800\text{--}1000 \text{ mg}\cdot\text{L}^{-1}$, increased VFAs results in pH decrease, and then FAN decreases, ammonia inhibition is thus mitigated partly (Fotidis et al., 2014; Nielsen and Angelidaki, 2008). Ammonia, VFAs and FAN form a mutual inhibition system for methanogens acclimatization as “inhibited steady state” (Angelidaki and Ahring, 1993). The state could be regulated by spatial and temporal coordination among VFAs, ammonia and carbonic acid in the methanogenesis reactor. If provided relative higher pH, carbonic acid would retain more in the methanogenesis reactor which results in a higher carbonate alkalinity (Braun et al., 1981). The carbonate combined with ammonia and VFAs could thus form a self-regulation pH buffer which could provide a more stable pH environment for the AD system. By periodically decreasing FAN concentration, ammonia acclimatization could be enhanced and ultimately result in a higher COD removal rate over 99% in this study. As ammonia inhibition was acclimated, ammonia would become a critical part of the ternary self-regulation pH buffer system rather than major inhibitor in the high rate AD system.

4. Conclusions

This study demonstrates that the biogas-pH strategy, basing on gas-liquor two phase monitoring and dynamic kinetics thresholds controlling, allows for an AnMBR operating with doubled OLR ($11.81 \text{ kgCOD}\cdot\text{kgVSS}^{-1}\cdot\text{d}^{-1}$) and halved effluent COD ($253.4 \text{ mg}\cdot\text{L}^{-1}$) when it treats high COD wastewater without adding alkalinity. The methane production kinetics and pH titrations were used as effective methods for determined the thresholds of biogas-pH strategy, which were biogas production rate $>98 \text{ Nml}\cdot\text{h}^{-1}$ preventing overload and $\text{pH} > 7.4$ preventing under-

load. Using biogas-pH strategy, AnMBR formed a “pH self-regulation ternary buffer system” containing VFAs, ammonia and bicarbonate which promoted pH over 7.4 and hence enhanced carbon dioxide seizing.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2015.12.010>.

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