Thermal pretreatment to enhance biogas production of waste aerobic granular sludge with and without calcium phosphate precipitates

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ABSTRACT

To develop aerobic granules based sustainable wastewater treatment, it is necessary to view wastewater treatment process and excess sludge treatment as a whole to evaluate resource recovery and sustainability. We thus investigated in this study how mineral characteristics of aerobic granules with/without calcium phosphate precipitates for phosphorus removal in treatment process affect the excess sludge digestion for energy recovery. Steam explosion at 170 °C as an effective thermal sludge treatment approach was studied in parallel with normal thermal treatment in an autoclave at 70, 100 and 125 °C, respectively. A liner relationship was found between the thermal treatment temperature in the autoclave and biogas production of aerobic granules. The untreated granules with only 10% mineral content (G1) generated 30 % more biogas than the untreated granules with 39% mineral content (G2), but steam explosion is more effective to G2 with high mineral content and relatively poor methane yield potential. In addition, steam explosion improved methane production from G2 more compared with activated sludge although both untreated activated sludge and G2 had comparable methane production, i.e. around 0.235 L CH4/g VS. Therefore, steam explosion is potential to be used to increase methane production especially when the untreated granular sludge has low methane yield due to high mineral content. This work provides a good basis for a holistic evaluation of resource recovery based on aerobic granular sludge, i.e. combined energy recovery and phosphorus removal and recovery via CaP precipitates, and trade-off between different factors with steam explosion.

Keywords: aerobic granules, steam explosion, biogas production, calcium phosphate, phosphorus removal and recovery, biomineralization

1. INTRODUCTION

Aerobic granule sludge is an emerging technology to replace conventional activated sludge due to its compelling advantages particularly on simplified process, small footprint, less energy consumption,

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and distinctive granule characteristics for wastewater treatment (Sarma et al., 2017). Since it was reported in 1991 (Mishima and Nakamura, 1991) for the first time, intensive research has been done to advance this technology for real application. Now, this technology is at the stage of commercialization and more than 50 commercial aerobic granular sludge based wastewater treatment plants have been constructed or at different stages of construction in different countries. Compared with conventional activated sludge technology, aerobic granular sludge based full-scale wastewater treatment plant is able to reduce energy consumption by 58-63%(Pronk et al., 2015), and plant footprint by 75% (De Bruin et al., 2004). But as activated sludge technology, aerobic granular sludge also produces huge amount of excessive sludge for management. At Garmerwolde wastewater treatment plant with aerobic granular sludge technology treating 28,600 m^3/day municipal wastewater, 3900 kg excess granular sludge was produced per day (Pronk et al., 2015). Anaerobic digestion of excess sludge is one of the most environmentally friendly option, which has been implemented widely for energy recovery as well as sludge management. With the considerable potential to construct more aerobic granular sludge plants to move towards more sustainable wastewater treatment, energy recovery from excessive granular sludge via digestion is very important to evaluate the net energy input or output of this technology from the holistic point of view including both wastewater treatment process and energy recovery process via digestion. However, almost all studies on aerobic granules focused on the wastewater treatment process instead of excessive granular sludge digestion, which leads to the lack of data to do holistic energy balance. A few recent papers started to pay attention to this problem, and their studies showed that aerobic granular sludge was able to be digested for biogas production just as activated sludge, but biogas production results from aerobic granular sludge (AG) are not very consistent when compared with activated sludge. Bernat et al. reported 1.8 time lower biogas potential of aerobic granules which was speculated due to high fibrous materials in AG (Bernat et al., 2017). However, equivalent anaerobic biodegradability between AG (33% and 49%) and activated sludge (30-50%) was found (Val del Rio et al., 2011). These contradictory results suggest that one or more key factors about aerobic granular sludge which might affect biogas production have been neglected. The most distinctive difference between aerobic granular sludge and activated sludge is sludge characteristics with different compactness and size, thus different chemical compositions. Aerobic granules treating different types of wastewater or treating the same type of wastewater but with different operational conditions can lead to different granule characteristics and chemical compositions, which might result in different anaerobic biodegradability. But this has not be explored so far.

Furthermore, with the adopted ambitious circular-economy strategy by the European Commission in 2015, and the continuous evolution of a more resource efficient bioeconomy, more valuable resource recovery from wastewater such as phosphorus attracted great attention(Egle et al., 2016). Due to the special three-dimensional and compact structure, and much higher extracellular polymeric substances, biologically induced inorganic precipitates were more easily formed in aerobic granules than activated sludge(Juang et al., 2010; Mañas et al., 2011; Liu et al., 2015). Biologically induced calcium phosphate precipitation in aerobic granules has been investigated as a very promising technology for effective phosphorus removal and recovery(Mañas et al., 2011; Manas et al., 2012), which directly leads to the increased mineral content in sludge. It is confirmed now that the mineral content affects granule characteristics(Ren et al., 2008; Lin et al., 2013; Liu et al., 2015), but it is completely unknown on how this changed sludge characteristics further affect biogas production in the downstream. This poses a great challenge to evaluate the integrated energy recovery, and phosphorus removal via the combined biomineralization and recovery as well as the trade-off between them. To address the research gap identified on this, it is very necessary and essential to investigate biogas production of aerobic granular sludge with and without calcium phosphate precipitates.

It is well known that the biodegradability of activated sludge for digestion is relatively low, which is only around 30-50% (Bougrier et al., 2008). Thermal hydrolysis pre-treatment is thus used as an enhancement approach for improved biogas production from sludge. The thermal pre-treatment has been not only investigated intensively in the lab, but also applied in full-scale wastewater treatment plants (Chauzy et al., 2008; Carrere et al., 2010). Among different thermal hydrolysis pre-treatment technologies, steam explosion is believed as one of the most effective options, which was implemented in full-scale plants since 1995 by CAMBI (Kepp et al., 2000), and demonstrated improved biogas production, and improved sludge dewaterability(Kepp et al., 2000) .. Based on very limited studies on biodegradability of aerobic granules, the biodegradability of aerobic granules is equivalent to or even much less than activated sludge(Val del Rio et al., 2011; Bernat et al., 2017). Despite of plenty of research on thermal pre-treatment to activated sludge or primary sludge, there is much less on aerobic granular sludge as aerobic granules sludge is a relatively emerging technology. So far, there lacks of any research on steam explosion on aerobic granular sludge for biogas production enhancement although it is easy to be adopted due to the technology maturity.

This study thus aims to investigate biogas production of waste aerobic granular sludge with and without calcium precipitates for phosphorus removal, and the effects of steam explosion pretreatment on the enhancement of the biogas production from sludge. To further the understanding of thermal treatment effects on biogas production from aerobic granules with different mineral contents, conventional thermal treatment was conducted as well. In addition, the biogas production from conventional activated sludge with/without steam explosion was compared to explore the potential of excess aerobic granular sludge for energy recovery.

2. MATERIALS AND METHODS

2.1 Reactor operation treating wastewater with aerobic granular sludge

Two sequencing batch reactors, R1 and R2, with a working volume of 2.6 L were used to treat synthetic wastewater with aerobic granular sludge at two different water hardness levels and phosphate levels to get different mineral contents in aerobic granular sludge. Both reactors were operated with a 3 h cycle, which consisted of 10-minute feeding, 2-minute settling, 1-minute discharging and aeration in the remaining period. The effluent was discharged from the reactor middle port, corresponding to 50% volume exchange ratio. 2.5 L minute^{-1} air was supplied from the bottom of reactors. The temperature during the experiment was not controlled, which ranged from 8°C to 16 °C. Synthetic wastewater was prepared with COD concentration at 1200 mg/L, NH_4^+-N at 60 mg/L, PO_4^{3-}-P at 12 mg/L in R1 and at 60 mg/L in R2, other micronutrients and trace elements same as that by Smolders et al. (1995). Since the hardness level of tap water in Southampton, UK is very high, synthetics wastewater fed into R1 was prepared by mixing DI water with tap water in a ratio of 3:1 to get calcium concentration at around 25 mg/L while the wastewater fed into R2 was prepared with tap water directly, in which calcium concentration is around 100 mg/L. The only operational difference between R1 and R2 are calcium concentration in the wastewater due to different water hardness levels and phosphorus concentrations. Phosphorus removal was observed concurrently with the increase in the mineral content in aerobic granules in R2. Aerobic granules from R1 was denoted as G1 while aerobic granules from R2 was named as G2 for easy description in the paper.

After two reactors reached the stable state, i.e. after 20 days with relatively stable mineral contents and SVI_5, granules were collected periodically and stored at 4 °C until the end of operation. Before granules were used for the subsequent experiments, stored granules were mixed evenly but mildly to ensure homogeneity.

2.2 Batch calcium phosphate precipitation

Batch tests were carried out to assess the phosphate removal mechanism. pH of synthetic wastewater to R1 and R2 without sludge, respectively, was adjusted to 9 and then was aerated in beakers for 60 min for phosphate precipitation with Ca. Samples were taken every minute in the first 5 minutes and less frequently during the remaining period, for phosphorus measurement to evaluate phosphorus removal rate via chemical CaP precipitation only without the participation of sludge.

2.3 Thermal pretreatment of aerobic granular sludge and activated sludge by steam explosion and autoclave, respectively

Waste activated sludge (WAS) was collected from Millbrook sewage work in Southampton, UK for the comparison with aerobic granular sludge. To avoid the effects of soluble chemicals from wastewater, raw granular sludge G1 and G2 was washed with DI water prior to thermal treatment at different temperature, so the concentration of all soluble chemicals in the liquid of raw granular sludge is 0. WAS, G1, and G2, respectively, were thermally pre-treated by CAMBI at 170 °C with steam for 30 minutes at the corresponding vapour pressure using pilot scale steam explosion apparatus (Cambi, Asker, Norway). The steam explosion apparatus was equilibrated to required temperature prior to the addition of material in order to reduce temperature fluctuation during actual explosion. The apparatus was pressurised and exploded several times to ensure the removal of all material from apparatus. In addition, thermal hydrolysis pre-treatment of G1 and G2 was conducted in a lab autoclave (Selecta, Barcelona, Spain) at 70, 100 and 125 °C for 30 minutes, respectively. Although the sludge was treated thermally at pre-set temperature for 30 minutes, the whole heating and cooling period in the autoclave lasted for a couple of hours roughly and the higher pre-set temperature resulted in a bit longer period for heating and cooling. Because the liquid fraction after steam explosion is much more than that after autoclave, the liquid fraction from steam explosion treated G1 and G2 was discarded without dosing into anaerobic digester to ensure an equivalent sludge volume and the sludge to inoculum VS ratio with the sludge samples treated at other temperatures in the autoclave. The thermal treatment conditions for anaerobic digestion is summarized in Table 1.

2.4 Batch anaerobic digestion of sludge

Untreated sludge and thermally pretreated sludge were digested in 590 ml bioreactors at 37 °C. The sieved digestate from the anaerobic digester at Millbrook Sewage Work, Southampton, UK, was inoculated into the bioreactors. The biogas was collected by displacement of a 20% saturated solution of sodium chloride acidified to pH 2 in calibrated glass cylinders to minimize solubilisation of gases(Soto et al., 1993; Borja and Banks, 1995). Vapour pressure and salt solution density were taken into account in correction of gas volumes to standard temperature and pressure (101.325 kPa, 20 °C). Biogas sample from each bioreactor was taken periodically for biogas composition analysis. All sludge digestion was carried out in duplicate. Meanwhile, the blank with only inoculum and the positive controls with cellulose were conducted. The biogas or methane production from the blank experiments without substrate addition was subtracted to calculate the biogas or methane production from substrate, i.e. sludge. In addition, the positive controls with cellulose was digested in triplicates/duplicates as positive controls to assess test validity as well as to calibrate the assay results carried out from different batches.

2.5 *Kinetic study of anaerobic digestion of aerobic granular sludge and activated sludge*

To determine the kinetics constants, the specific methane production was modelled using Gompertz model (i.e. the first-order model) and modified Gompertz model with the consideration of lag phase. Gomperts model was shown as below:

$$\mathrm{Y} = Y_{max}(1 - \exp(-kt)) \quad (1)$$

Where Y is the cumulative methane yield at time t, Y_{max} is the methane yield potential of the substrate and k is the methane production rate constant.

For some substrates, lag phase was noticed for methane production. The lag phase (λ) can be calculated with the help of modified Gompertz model. The equation for modified Gompertz model is given in the following equation.

$$\mathrm{Y} = Y_{max}\exp\{-\exp\left[\frac{R_b}{Y_{max}}(\lambda - t) + 1\right]\} \qquad (2)$$

Where Y is the cumulative methane yield at time t, Y_{max} is the methane yield potential of the substrate; R_b is the maximum methane production rate; λ is the lag phase, t is the time in days.

2.6 Analytical method

For aerobic granular sludge reactor operation, VSS, TSS, VS, TS, SVI, COD, phosphate and TKN were analysed in accordance with standard methods (APHA, 2012). MLSS in the reactors was measured by using density method (Beun et al., 1999). Ammonium was measured by Spectrophotometric method (3000 series, Cecil Instruments Ltd., UK) described in the manual BSI (1984) Volatile fatty acid (VFA) from the thermally treated sludge samples was analysed by a GC-2010 (Shimadzu, Milton Keynes, UK), using a flame ionization detector and a capillary column type SGE BP-21, based on the Standing Committee of Analyst procedure (SCA, 1979). Three standard solutions containing 50, 250 and 500 mg/L of acetic, propionic, iso-butyric, n-butyric, iso-valeric, valeric, hexanoic and heptanoic acids were used for VFA calibrations, and the total VFA concentration was expressed as COD mg/L.

The gas composition of biogas produced from the anaerobic digestion was quantified using a GC-Star 3400 CX, (Varian Ltd, Oxford, UK). The device was fitted with a Hayesep C column and used argon as the carrier gas at a flow of 50 mL minute^{-1} with a thermal conductivity detector. The biogas composition was calibrated with a standard gas containing 65 % CH4 and 35% CO2 (v/v). The biogas samples were analysed in duplicate with the injection of 5 ml biogas into the GC each time.

A multi collector emission spectrometer ICP-MS X-SERIES 2 (Thermo Fisher Scientific, Bremen, Germany) was used to quantitatively measure the elemental composition of the sludge. After overnight drying at 105 °C, the dry sludge was ground into powder, from which 50 mg powder was digested with 2 mL of aqua regia (1:3 mixture of 68% nitric acid and 36% hydrochloric acid) and 0.5 mL perchloric acid (68%) in a Teflon digestion vessel overnight on a hotplate (150 °C). The digestion vessel was then opened for sample to dry, after which 10 mL of concentrated hydrochloric acid (36%) were added. Prior to ICP-MS analysis, the sample was dried again and 3% nitric acid was added. Only the main elements contained in the synthetic feedstock solution (i.e. Na, Mg, P, K, Ca and Fe) were investigated and data was processed using Plasmalab software.

3. RESULTS AND DISCUSSION

3.1 Granulation and performance of granular sludge treating wastewater with two different calcium and phosphorus levels

The same operational conditions were adopted except for different Ca^{2+} and phosphate concentrations in two reactors, but granulation showed different speed. As shown in Figure 1, SVI_5 dropped to 56 mL/g and SVI_{30}/SVI_5 reached 92% on day 3 in R2 concomitant with the observation of dominant granules. However, SVI_{30}/SVI_5 in R1 reached above 90% on day 5, 2 days slower than that in R2. In addition, it is noteworthy that SVI_5 in R1 was still above 100 ml/g until day 9 although granules were formed and dominant on day 5. This suggests that SVI_5 alone cannot be used as the single parameter to determine the sludge granulation. Due to high Ca and phosphorus concentrations in R2, CaP precipitates were formed, which benefits granulation and granule growth by forming nucleus for bacteria to attach. This is similar to the initial stage of biofilm formation with CaP precipitates as carrier media, which demonstrates here to be 2 days faster than the auto-aggregation of bacteria to form granules in R1. The enhancement of granulation by dosing ions such as Ca, Mg, and Fe reported in literature is to essentially form inorganic precipitates to stimulate the formation of biofilm first to initiate the granulation. Therefore, for the wastewater containing higher inorganic metal ions, the granulation could be faster and easier(Liu and Tay, 2015). In addition, the settling ability of formed granules indicated as SVI_5 at the initial stage such as the first 10 days without inorganic precipitation in R1 is much higher than that in R2. However, over the operation time, the difference of SVI_5 between two reactors become narrower and narrower, and SVI_5 in both R1 and R2 is lower than 50 ml/g because granules in R1 became more compact over the time due to the multiplication of bacteria locally in granules. After day 20, the mineral content of sludge stabilized at around 40% in R2 and 10% in R1 as shown in Figure 2.

Although the influent COD to both reactors were 1200 mg/L, and cycle time was 3 hr, resulting in organic loading rate as high as 4.8 g/(L·d), COD removal efficiency for both reactors reached above 85%. In addition, total nitrogen removal efficiency was above 75%, which was removed by assimilation to a great extent due to low influent ammonium/COD ratio. Since there is no alternating anaerobic and aerobic phases in R1 and R2, there is no chance for polyphosphate accumulating organisms (PAOs) to be enriched in R1 and R2 for phosphorus removal. However, after 20-day operation, phosphorus removal rate in R1 at the steady state was 43±5% while it reached 68±4% in R2 although the influent P in R2 was as high as around 60 mg/L. The batch precipitation at pH 9 with the medium similar to that to R1 and R2 but without sludge showed less than 10% and 36% phosphorus removal rates, respectively, by chemical calcium phosphate precipitation, suggesting that there is other mechanisms involved for phosphorus removal. If it is assumed that other phosphorus removal except for chemical precipitation in R1 is by assimilation, and R1 and R2 have the similar amounts of phosphorus assimilation, 20mg/L phosphorus in R2 is removed by biologically induced CaP precipitation in aerobic granules as reported by Manas(Mañas et al., 2011) . The biologically induced CaP precipitates in aerobic granules in conjunction with the possible adsorption of chemically precipitated CaP by granules led to the accumulation of CaP in aerobic granules in R2, and thus the increased mineral content. During the long-term operation period, the mineral content in G2 from R2 stabilized at around 40% although there was continuous sludge waste. Due to the high mineral content in G2, the structure of G2 was very compact with SVI_5 as low as 11 ml/g while SVI_5 of G1was around 50 mL/g.

3.2 Characterization of granules with two different calcium and phosphorus levels

Elemental analysis results of the collected granular sludge are shown in Table 2 and compared with literature. Except for elements P and Ca, the levels of minerals in G1 and G2 are more or less same and the mineral levels in aerobic granular sludge in this study are equivalent to those treating different types of wastewater under sequential batch and continuous operational modes (Liu et al., 2015). However, P and Ca contents in G2 with higher water hardness level and phosphorus concentration are 5.1 times and 8.5 times higher than those in G1, respectively. 5.61% P content in G2 is much higher than the conventional activated sludge with around 1% P and that of G1 with 0.9% P. Actually, Ca and P contents in waste G2 are comparable with those in sewage sludge ash after incineration(Cohen, 2009), which indicates great opportunity for phosphorus recovery from G2. The accumulation of both P and Ca in G2 suggests the precipitates of CaP, and XRD analysis further proved the presence of crystals of hydroxyapatite, haneuite and calcite.

Calcium is very easy to precipitate in aerobic granular sludge in the forms of $CaCO_{3(\text{Liu et al., 2015})}$ or CaP via biomineralization(Mañas et al., 2011) as the microenvironment in aerobic granules could become supersaturated for the precipitation due to microbial activity, mass transfer gradient and higher EPS contents in granules(Mañas et al., 2011). It has been reported extensively that EPS contents in aerobic granular sludge is much higher than that in activated sludge to stimulate granulation and maintain the stability of granules(Liu et al., 2004). It was also reported that EPS contributes to phosphorus removal (Cloete and Oosthuizen, 2001). Mineral precipitation is affected by reactor operation mode, calcium concentration in the water, and other microbial metabolism for degrading different substrates. When water hardness level is high particularly with high calcium concentration, precipitation is easy to occur in aerobic granules. In this study, calcium concentration in wastewater fed to R2 was 100 mg/L, which directly facilitates the calcium phosphorus precipitation chemically or biologically induced in granules. Precipitation of CaP in aerobic granules even with lower phosphorus concentration was also observed by other researchers (Mañas et al., 2011; Li et al., 2014). Phosphorus removed by aerobic granules with enriched PAOs is believed to be a combination of biological phosphorus uptake by poly-phosphate accumulating organisms and biologically induced phosphorus precipitate (De Kreuk et al., 2005). Although no PAOs were enriched in aerobic granules in this study, phosphorus was removed by both chemical and biological induced CaP precipitates in R2, for which high calcium concentration in wastewater is critical.. Thus, in different areas with different water hardness levels particularly with different calcium concentrations, aerobic granules could have different levels of mineral contents due to the precipitates of CaP or CaCO3.

Although minerals themselves as inorganics do not contribute to sludge biodegradability directly, the accumulation of minerals could change the chemical compositions of sludge by changing the granular sludge’s compactness, and size, which further changes mass transfer in the granules, microbial activity, microbial community and EPS contents. From our previous work, it was found that with the increase of minerals in granular sludge from 20% to 80%, extracellular polysaccharide in granules reduced by 80% (Liu et al., 2015). Therefore, it is very necessary to investigate the biodegradability of granules with different mineral contents.

3.3 Soluble chemicals after thermal hydrolysis pretreatment of aerobic granules at different temperatures

To study the thermal treatment effects on granules, granular sludge from R1 and R2 was thermally treated in the lab autoclave at 70, 100, 125 °C, respectively. . After thermal pre-treatment at 70 °C, the appearance of aerobic granular sludge still looked exactly same as before the treatment, i.e. maintaining the intact granule structure and easily separated from liquid. However, after thermal pre-treatment at 100°C and 125 °C, vast majority of granules disintegrated and only a small amount of granule fragments were observed. Meanwhile, the sludge became extremely gelatinous and lost its fluidity at ambient temperature. Some sludge erupted from the bottle at the thermal treatment temperature of 125°C while this did not happen at100°C, suggesting high viscosity of sludge and less heat uniformity at 125°C. The gelatinous compactness structure of aerobic granular sludge at 125°C implies the handling difficulty of sludge for the subsequent treatment, which is not an ideal treatment temperature in terms of rheology. This phenomenon that aerobic granular sludge becomes gelatinous after thermal treatment in the studied range similar to the observation by Val del Rio et al.(Val del Rio et al., 2011), who reported that aerobic granular sludge presented a viscous aspect similar to that of a gel after thermal pre-treatment. But in their report, sludge showed gel compactness structure with the thermal treatment from temperature 60 to 115°C and reached the maximum gel compactness structure at 115°C. Obviously, the temperature for aerobic granular sludge to become gelatinous in this study is much higher than that reported by Val del Rio(Val del Rio et al., 2011) although the similar thermal treatment methods, i.e. autoclave, was used. This difference might greatly depend on the specific characteristics of aerobic granular sludge, which are from different operational conditions treating different types of wastewater. For activated sludge, however, Bougrier et al. observed the opposite trend that sludge volume index (SVI) decreased with the rise in treatment temperature and apparent viscosity of sludge after thermal treatment reduced accordingly with the temperature increase(Bougrier et al., 2008). Other studies on the rheology of activated sludge also found that both storage moduli and loss moduli decreased with the increase in thermal treatment temperature (Farno et al., 2016; Feng et al., 2018), showing less viscosity and lower resistance to flow after thermal treatment. This repeatedly confirmed contrast on sludge rheology after thermal treatment between activated sludge and aerobic granular sludge, which demonstrated that chemical compositions in these two types of sludge are distinct. Thus, it suggests the necessity to investigate the digestion of aerobic granular sludge and relevant thermal pre-treatment. .

EPS is one of the most important factors to affect sludge viscosity after thermal treatment. The most widely reported difference in terms of chemical compositions between activated sludge and aerobic granular sludge is EPS(Liu et al., 2004), which is at least 3 time higher in aerobic granular sludge than that in activated sludge. For example, Adav and Leereported 394-694 mg EPS/g VSS in aerobic granules with different extraction methods but it was only 182-205 mg EPS/g VSS in activated sludge (Adav and Lee, 2008). The large release of EPS and property change of EPS at higher temperature in aerobic granules could exacerbate the sludge fluidity, leading to different trends of viscosity at high tempreture.

To investigate the hydrolysis and solubility of sludge after thermal pre-treatment, NH_4^+-N, TKN, PO_4^{3-}-P, sCOD, VFA in the liquid after thermal treatment at 70 °C, 100 °C and 125°C were analysed. After thermal treatment at different temperatures, it was found that NH_4^+-N and PO_4^{3-}-P concentrations from G1 and G2 have no much difference, and NH_4^+-N is in the range of 1.32-2.35 mg/L and PO_4^{3-}-P is in the range of 0.50-2.65 mg/L for all treated sludge. VFAs are at very low levels such as 100-235 mg COD/L. TKN and soluble COD, however, increased as shown in Figures 3a and 3b when thermal pre-treatment temperature increases from 100 °C to 125 °C. This indicates that thermal treatment can enhance the solubility of sludge, but the soluble chemicals at this stage are still present in the forms of large organic molecule such as protein and carbohydrate with low NH_4^+-N, PO_4^{3-}-P and VFA concentrations. These results are consistent with what Ferreira et al.(Ferreira et al., 2014) found for the sludge thermal treatment. Although sCOD and VFA were increased after thermal pre-treatment in this study, the concentrations of sCOD ranges from 150mg/L to 450mg/L, and VFA ranges from 100-235 mg/L, which are still relatively low compared with values reported by Bougrier et al(Bougrier et al., 2008). When sCOD and TKN of G1 and G2 after thermal treatment were compared, it was found that sCOD from G2 was always higher than that from G1 while TKN from G2 was always lower than that from G1 at different thermal treatment temperature. These opposite trends of sCOD and TKN indicates that thermal treatment to G2 at 125°C released more soluble carbohydrates than protein compared with G1, which further suggests that chemical compositions of G1 and G2 could be different.

3.4 Batch anaerobic digestion of aerobic granular sludge treated with autoclave and steam explosion, respectively

Figure 4a shows the cumulative biogas production of two types of untreated aerobic granular sludge (assume 20°C) and aerobic granular sludge with thermal pre-treatment at 100°C, 125°C and 170°C, respectively, at the end of batch anaerobic digestion. The cumulative biogas production at the end of batch anaerobic digestion could also be understood as biogas yield based on volatile solid. From Figure 4a, it can be seen very clearly that the high mineral content in aerobic granular sludge affected the biogas yield negatively. Untreated G2 with 39% mineral content generated 30% less biogas yield. With thermal hydrolysis pre-treatment, biogas yields of both G1 and G2 were enhanced, which means that thermal pre-treatment can improve aerobic granular sludge biodegradability for more biogas production. This is in agreement with results studied on the effects of thermal pre-treatment on biogas production from activated sludge (Bougrier et al., 2008; Carrere et al., 2010) and aerobic granular sludge (Val del Rio et al., 2011).

Furthermore, it was very interesting to find from Figure 4a that the biogas yields at 20°C, 100°C, and 125°C had a good linear relationship for both G1 and G2 with granular sludge treated in the autoclave. This is the first time for this linear relationship between biogas production and thermal treatment temperature to be reported for aerobic granules, which is meaningful as this linear relationship could be easily used to estimate the biogas production at thermal treatment temperature which is not carried out. To validate this finding and its reproducibility,the methane production data produced by Val del Rio et al.(Val del Rio et al., 2011) from the published paper was extracted, and fitted in Figure 4b. Val del Rio et al. investigated the effects of thermal-treatment of aerobic granular sludge on anaerobic biodegradability with two types of aerobic granules, i.e. one fed with pig manure and the other fed with municipal wastewater, at thermal treatment temperature range from 20 to 210 °C in an autoclave(Val del Rio et al., 2011). Both types of granules fed with pig manure and granules fed with municipal wastewater, respectively, had higher methane yield at elevated thermal pre-treatment temperature although granules fed with pig manure had reduced methane yield if the thermal treatment temperature was above 170 °C. When their data were fitted to correlate methane yield with thermal pre-treatment temperature, a good linear relationship was found as well for both types of granules as shown in Figure 4b. The linear relationship shown in Figure 4b is in good agreement with thermal pre-treatment from 20 to 125°C in the autoclave in this study although the granules from Val del Rio et al. were cultivated to treat different types of wastewater at different operational conditions(Val del Rio et al., 2011). This suggests that a good prediction about biogas or methane yield at an unknown temperature could be obtained by extrapolation or interpolation based on the known data when thermal pre-treatment temperature is lower than 170 °C . From the extrapolation based on the linear fit at 20, 100, and 125°C in Figure 4a, biogas yield is expected to be as 0.568 L biogas/g VS for G1 and 0.511 L biogas/g VS for G2, respectively, after thermal pre-treatment at 170 °Cif the autoclave was used. The biogas yields after steam explosion at 170 °C, however, are much higher and they are 0.612 L biogas/g VS for G1 and 0.569 L biogas/g VS for G2, respectively. Since thermal pre-treatment at 170 °C in this study was carried out with steam explosion, it is believed that apart from the temperature effect, steam explosion plays extra role to enhance sludge biodegradability. Although steam explosion has been studied and proved to be able to enhance digestion of waste activated sludge (Kepp et al., 2000; Dereix et al., 2006), there is no such study on aerobic granular sludge so far. Also, there is no study to try to compare the effects between steam explosion and normal thermal treatment at the same temperature. This study shows the higher potential of steam explosion to enhance the anaerobic digestion of aerobic granular sludge.

From Figure 4, it can be seen that thermal treatment is effective to any type of aerobic granular sludge for improved biogas production regardless of the initial biogas yield. However, from the fitted lines in both Figure 4a and Figure 4b, it is found that the increase rates in biogas/methane yields, i.e. line slopes, are different for different types of aerobic granules with some having steeper increase than others. But the difference between biogas yields at elevated temperature became narrower, implying that thermal treatment at higher temperature produces more effects for the biogas enhancement to the sludge with the lower initial biogas yield. Therefore, thermal treatment is more applicable to aerobic granular sludge with relatively poor biodegradability.

3.5 Comparison of anaerobic digestion between aerobic granular sludge and activated sludge treating municipal wastewater with steam explosion treatment at 170 °C

In this study, waste activated sludge was digested as well to compare with G1 and G2. The mineral content is 10% in G1 and 39 % for G2, while it is 15% in activated sludge. It can be seen from Figure 5 that methane yield based on per gram volatile solid by G2 is similar to that of activated sludge, but 32% lower than that of G1 although the similar wastewater was treated and the same reactor operational conditions were used. G1 has similar mineral content with activated sludge (AS) from the local sewage plant, but methane yield of G1 is much higher than AS. From the results reported by Val del Rio et al., it is found that granules with mineral content of 43% fed with urban wastewater had 49% biodegradability while granules with mineral content of 8% fed with pig manure had 33% biodegradability (Val del Rio et al., 2011). This indicates that the difference in mineral content is not the essential reason to cause this difference. The possible reason is that different operational strategies were used to treat wastewater. For example, Millbrook sewage work where activated sludge was collected uses Bendenpo process to treat wastewater with organic loading rate of 0.8 g COD/(L·d) while SBRs in this study were used to treat wastewater with an OLR of 4.8 g COD/(L·d). With the same organic loading rate, same hydraulic retentions time and the same type of wastewater for G1 and G2 in this study, however, the mineral contents such as CaP in aerobic granular sludge did make difference in terms of methane production. High mineral contents results in the more compact structure with SVI of G1 at 46 mL/g while 11 mL/g for G2, leading to more compact structure of G2. This more compact structure, as pointed out above, could change mass transfer in the granules and chemical compositions of granular sludge, and thus biogas production. For aerobic granular sludge rector operation, although it was suggested to dose metal ions to induce mineral precipitates to accelerate granulation or to maintain the long term structure stability of granules (Jiang et al., 2003; Juang et al., 2010), the benefit of this has to be weighed with methane yield if the subsequent digestion of excess aerobic granular sludge was considered. In addition, if biologically induced CaP precipitation was used to remove and recover P from wastewater as recommended (Mañas et al., 2011; Manas et al., 2012; Lin et al., 2013; Huang et al., 2015; Zhang et al., 2015) or chemical precipitation of CaP was combined in the biological wastewater treatment process(Clark and Stephenson, 1999), the methane yield of the sludge with higher mineral content in the digestion stage would be compromised. But steam explosion is a very effective way to improve it.

Table 3 provides the specific data for comparison of methane yield of sludge. When WAS was used as baseline to compare with aerobic granular sludge, it was found that G1 produces 129% methane per VS while G2 produces 97%, equivalent to WAS. Thus, it is fair to say that if methane production potential of aerobic granular sludge is higher than WAS or not greatly depends on granule characteristics and operational conditions of AG reactors. This could explain well why Bernat et al. (2017) reported 1.8 time lower biogas potential of aerobic granules while Val del Rio et al. (2011) found equivalent anaerobic biodegradability between AG (33% and 49%) and activated sludge (30-50%).

After steam explosion, G1 still exhibits the highest methane yield. When untreated sludge was used as baselines for comparison, it was found the steam explosion is the most effective to G2 with the highest increase in methane production while it is the least effective to G1, indicating that steam explosion is probably more effective to raw sludge with less methane yield potential. It has been reported by Bougrier et al. (2008) for activated sludge and by Val del Rio et al.(Val del Rio et al., 2011) for aerobic granules that thermal treatment is the most effective to the sludge with the poorest methane production. However, it has to be pointed out that although raw AS and G2 has equivalent biogas production (100% and 97%), G2 got 155% methane yield while WAS's was only 139% after steam explosion. The comparison between AS and G2 before and after steam explosion suggests that the effectiveness of thermal treatment is dependent on not only the methane yield potential of the raw sludge, but also the characteristics of raw sludge. In this study, it is obvious that G2 possesses the more favourable characteristics for enhanced methane production after steam explosion compared with AS, implying that aerobic granular sludge might have higher methane production potential.

3.5 Kinetic study of anaerobic digestion of aerobic granular sludge and activated sludge with/without steam explosion The kinetic parameters for each substrate were evaluated by best fitting the experimental data on cumulative methane production and substrate added with the least squares fitting method. The modelled lines with Gompertz model were shown in Figure 5 and kinetics values obtained for these parameters are shown in Table 4.

Results suggest that both Gompertz model and modified Gompertz model are able to be used to model methane production for both untreated or steam exploded aerobic granular sludge and activated sludge with the coefficient of determination R^2 at least 0.981. Modified Gompertz model is more accurate for the first 4 days with lag phase while Gompertz model fits best the experimental data without lag phase. In addition, Gompertz model provides a better fit after 4-day digestion, suggesting a more accurate prediction about the ultimate methane production. Therefore, it is suggested to use Gompertz model to predict the methane yield from aerobic granular sludge.

In addition, it can be seen from Y_{max} of raw sludge from Gompertz model in Table 4 that the biodegradability (i.e. from the methane yield potential) of AS, G1 and G2 was improved by steam explosion. However, the methane production rates k of three types of sludge were not increased correspondingly. This seems be inconsistent with the increase in biodegradability enhanced by steam explosion. The possible reason is that k in Gompertz model is not based on mass transfer and reaction mechanisms such as hydrolysis, acidogenesis, acetogenesis and methanogenesis (Huiliñir et al.) like what IWA AD model No. 1 (ADM1) does(Appels et al., 2008), and it is just a generalized rate constant without the precise physical meaning. Different k values were found by different researchers using Gompertz models on digestion such as 0.017-0.040/day for fish waste(Kafle et al., 2013), 0.087-0.210/day for Vinasse(Budiyono and Sumardiono, 2014), and 0.044-0.094 for co-digestion of pig manure with WAS(Zhang et al., 2014) while it is 0.266-0.432 in this study. Although the substrate type could be one factor to affect k value, another important factor that could not be neglected for batch digestion is that anaerobic digestion conditions such as substrate/inoculum ratios and nutrients also affect digestion rate. Therefore, it needs to be careful when using k to interpret the experimental data particularly when compared with other literature without identical key digestion conditions. But Gompertz model is very simple to use and fits in the experimental data well. Y_{max} in Gompertz model is able to be used perfectly to compare the methane yield potential and biodegradability of different substrates.

4. CONCLUSIONS

Based on the research work done in this study, the conclusions as below are drawn:

- Chemical precipitation and biologically induced precipitation of calcium phosphate for phosphorus removal occurred at the same time to increase the mineral content of aerobic granule to 39% with around 100mg/L calcium and 60 mg/L phosphorus concentrations.

- The increased mineral content in aerobic granules by CaP (i.e.39%) resulted in 30% less methane production compared with those with mineral content of 10% at the similar operational conditions.
- A liner relationship was found between the thermal treatment temperature in autoclave and biogas production of aerobic granules, and this conclusion can be applies to more wide ranges of aerobic granules treating different types of wastewater at different conditions for the estimation of biogas production at unknown treatment temperature with less work load.
- Steam explosion is more effective than a normal autoclave thermal treatment at the same temperature to enhance methane production of aerobic granules, and steam explosion improves methane production of aerobic granules more than that of activated sludge when these two types of untreated sludge have comparable methane production. Therefore, steam explosion is potential to be used to increase methane production especially when the untreated granular sludge has low methane yield due to high mineral content such as calcium phosphate from chemical or biologically induced precipitation for P removal and recovery.

This work for the first time correlates increased mineral content in aerobic granules such as calcium phosphate precipitation for phosphorus removal in wastewater treatment process (upstream) with energy recovery in the subsequent digestion process (downstream). In addition, the effectiveness study on steam explosion treatment for the improved methane production of aerobic granules is able to be served as reference for a decision if steam explosion is needed or not. Results in this study provides datasets and good basis for a holistic evaluation of resource recovery based on aerobic granular sludge, i.e. combined energy recovery and phosphorus removal and recovery via chemical or biologically induced precipitation, and trade-off between different factors including steam explosion.

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Tables

Table 1 Thermal pretreatment conditions of sludge for anaerobic digestion

Sludge	Thermal pretreatment	
	Temperature (°C)	Equipment
G1	70	Autoclave
	100	Autoclave
	125	Autoclave
	170	CAMBI (steam explosion)
G2	70	Autoclave
	100	Autoclave
	125	Autoclave
	170	CAMBI (steam explosion)
WAS	170	CAMBI (steam explosion)

Table 2 The mineral contents of aerobic granular sludge treating wastewater with two different water hardness and phosphorus levels at the same reactor operational conditions

	VS/TS	Na	Mg	P	K	Ca	Mn	Fe	Co	Ni	Cu	Zn
	%	(g kg^{-1} dry biomass)										
G1	90	5.42	1.90	9.21	2.62	19.77	0.025	0.34	0.009	0.009	0.086	0.009
G2	61	5.87	3.05	56.51	3.30	188.10	0.018	0.21	0.021	0.009	0.058	0.004
Granules[13]*	75	8.00	1.32	3.97	2.91	184.56	0.016	0.54	0.005	-	0.106	-
Granules[13]**	16	2.48	0.56	0.77	0.49	306.53	0.65	2.16	0.019	-	0.105	-

* Granuels from batch operation and ** granules from continuous operation from Liu et al. (2015)[13]

Table 3 Comparison of methane production between different types of untreated sludge and sludge after steam explosion at 170°C

Methane production from untreated sludge		Methane production from sludge after steam explosion at 170 °C	
Activated sludge (AS)	100%	Activated sludge (AS-170°C)	100%
Aerobic granules 1 (G1)	129%	Aerobic granules 1 (G1-170°C)	119%
Aerobic granules 2 (G2)	-97%	Aerobic granules 2 (G2-170°C)	109%

Methane production		Methane production		Methane production	
Activated sludge (AS)	100%	Aerobic granules 1 (G1)	100%	Aerobic granules 2 (G2)	100%
Activated sludge (AS-170°C)	139%	Aerobic granules 1 (G1-170°C)	128%	Aerobic granules 2 (G2-170°C)	155%

Note: 100% means that the methane production from this sludge is used as basis for comparison

Table 4 Kinetics parameters of Gompertz model and modified Gompertz model for CH_4 production from different types of sludge

Parameter	AS	G1	G2	AS-170	G1-170	G2-170
Gompertz model (First-order model)						
Y_{max} (L CH4/g VS)	0.239	0.308	0.232	0.348	0.401	0.372
k (d-1)	0.389	0.419	0.432	0.266	0.389	0.313
R^2	0.983	0.998	0.998	0.981	0.988	0.981

Parameter	AS	G1	G2	AS-170	G1-170	G2-170
Modified Gompertz model						
Y_{max}(L CH4/g VS)	0.266	0.298	0.225	0.316	0.380	0.344
R_b (L/d)	0.069	0.078	0.059	0.077	0.113	0.093
λ (d)	0.135	-0.228	-0.266	0.330	0.090	0.242
R^2	0.984	0.986	0.986	0.991	0.988	0.985

Figures

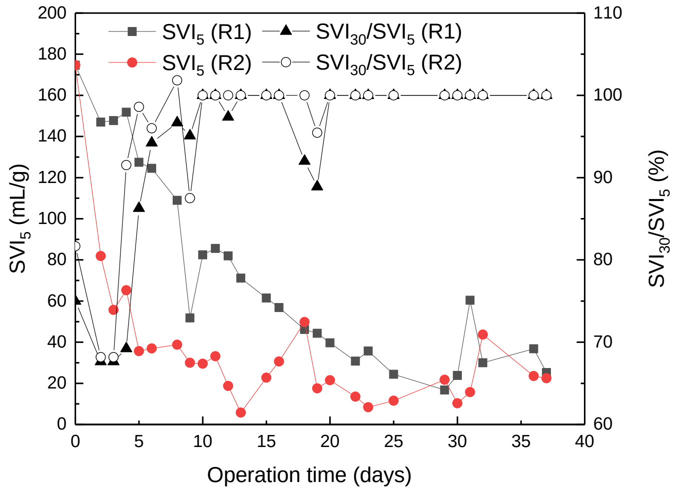


Figure 1. SVI_5 and SVI_{30}/SVI_5 profiles over the opertional time in two reactors with different calcium and phosphorus concentrations

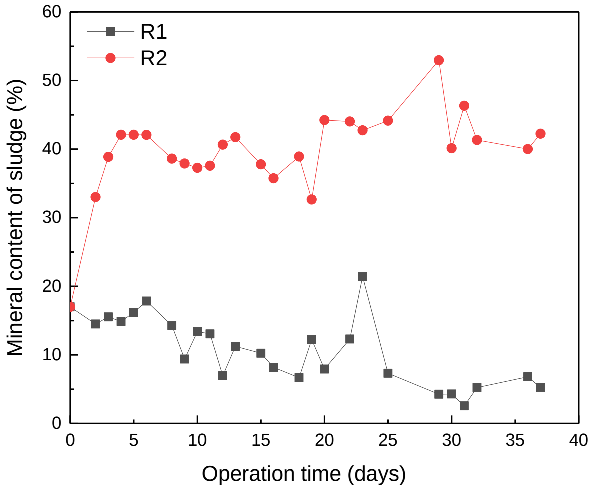


Figure 2. Sludge mineral changes over the operational time in two reactors with different calcium and phosphorus concentrations

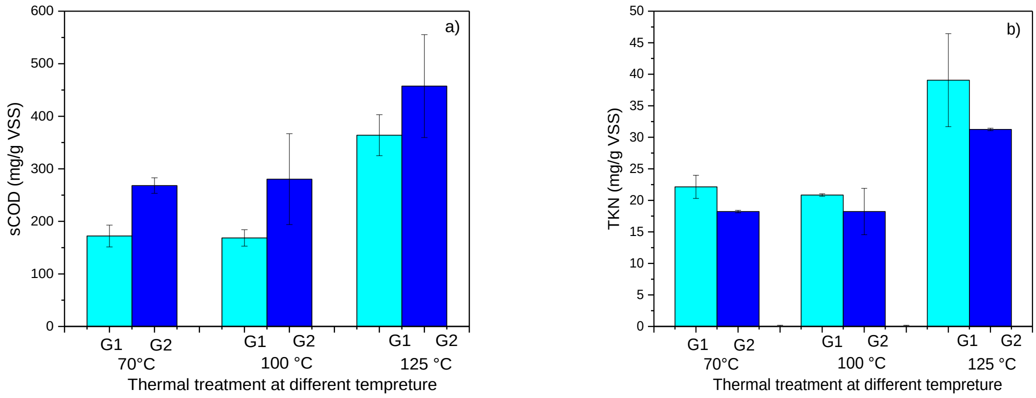
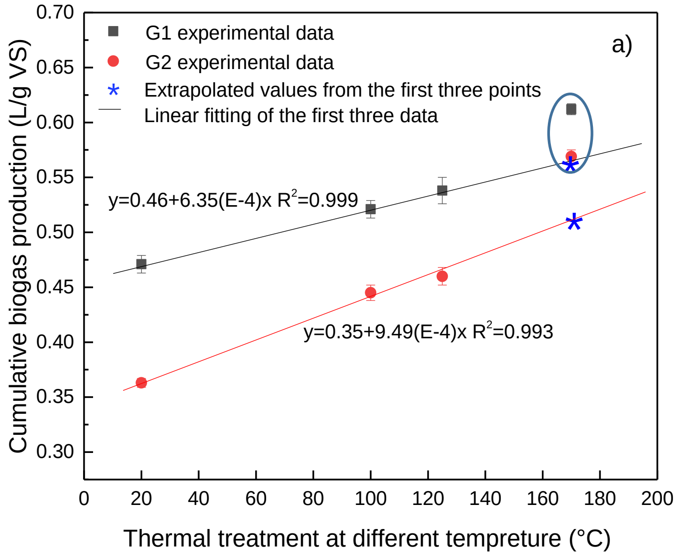


Fig.3 Soluble COD and TKN after thermal pre-treatment of granules (G1) from R1 and granules (G2) from R2 at 70, 100 and 125 °C



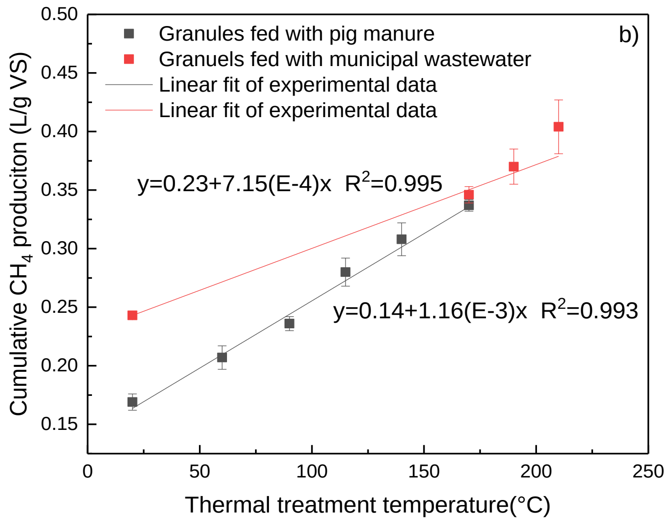


Fig.4 Cumulative biogas (or methane) production of untreated aerobic granular sludge (20°C) and treated aerobic granular sludge at different temperatures at the end of anaerobic digestion; a) results in this study, with two experimental data from the steam explosion at 170°C in the blue circle; b) results from Val del Rio et al et al (Water Research, 45(2011) 6011-6020).

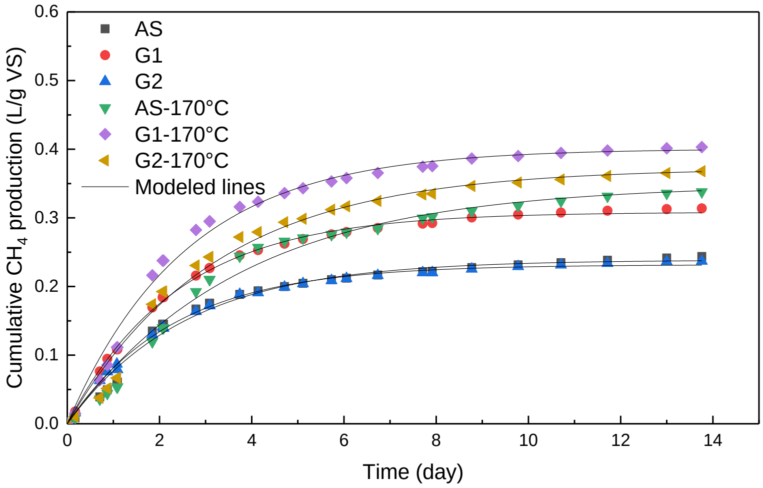


Fig.5 Cumulative methane production of untreated sludge and treated sludge with steam explosion at 170 °C, and simulated methane production with Gospertz model