

Effect of steam explosion on physicochemical properties of waste activated sludge and the performance of anaerobic digestion

Yan Zhang, Peng Han, He Liu, Lihui Zhang, Hongbo Liu and Bo Fu

ABSTRACT

The effect of steam explosion on physicochemical properties of sludge and the performance of anaerobic digestion (AD) was investigated. The steam explosion was conducted under different combinations of temperature and time, ranging 151–198 °C and 4–12 min respectively. The capillary suction time (CST) and viscosity of the sludge was increased with particle size decreased by improved hydrolysis temperature and prolonged hydrolysis time. The best sludge solubilization achieved was 41.3% under pretreatment condition of 198 °C and 4 min. Biogas production was enhanced with the improved sludge solubilization, and a linear correlation was found between biogas production and the severity factor ($\log R_0$) of steam explosion. However, the biogas productivity was reduced when the $\log R_0$ was increased from 3.79 to 3.96, probably owing to the generation of refractory organics during the high severity pretreatment. The temperature of 198 °C and the time of 8 min were the recommended operation parameters of steam explosion pretreatment for sludge AD, which could improve biogas production by 99.7 mL/g VS_{fed} . The pH and NH_4^+-N during sludge AD was increased by steam explosion pretreatment; however, no inhibition on biogas production was observed.

Key words | anaerobic digestion, biogas production, pretreatment, steam explosion, waste activated sludge

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NOMENCLATURE

AD	Anaerobic digestion	VS	Volatile solids
BC	Blank control	VS_{fed}	Volatile solids fed for anaerobic digestion before steam explosion
COD	Chemical oxygen demand	WAS	Waste activated sludge
CST	Capillary suction time	WWTP	Wastewater treatment plant
D50	Median diameter		
EC	Experimental control		
EPS	Extracellular polymeric substances		
FAN	Free ammonia nitrogen		
LF	Logistic function		
MG	Modified Gompertz		
SCOD	Soluble chemical oxygen demand		
SR	Solubilization ratio		
TF	Transference function		
TP	Total phosphorus		
TS	Total solids		
UASB	Up-flow anaerobic sludge bed		
VFAs	Volatile fatty acids		

INTRODUCTION

Waste activated sludge (WAS) is generated as a byproduct of biological wastewater treatment, and is characterized by high concentration of organic matters (Neumann *et al.* 2016). Owing to its characteristics and the considerable productivity, disposal of WAS is a critical issue accompanying wastewater treatment, but also provides an opportunity for energy and resources recovery. Anaerobic digestion (AD) could effectively achieve mass reduction, pathogen reduction, as well as energy recovery, and is one of the

most widely used sludge treatment technologies. A combustible biogas composed principally of CH₄ and CO₂ is produced by AD from organic substrate in the WAS via hydrolysis, acidogenesis, acetogenesis and methanogenesis. However, intracellular organic materials of the sludge are segregated by microbial cell walls, which are hard to degrade during hydrolysis, and often cause lowering of overall sludge digestion efficiency (Lee *et al.* 2017). Therefore, hydrolysis is regarded as the limiting step of AD and the limiting factor influencing biogas production (Gianico *et al.* 2013).

In order to speed up the reaction rate and enhance reaction efficiency of digestion, various pre-treatment technologies have been studied to overcome the drawback of hydrolysis, including physical technologies like thermal treatment (Bougrier *et al.* 2007), chemical technologies like alkaline (Lin *et al.* 2009) and acid (Devlin *et al.* 2011) treatment, Fenton (Pilli *et al.* 2016), and biological technologies like enzyme treatment (Yin *et al.* 2016). Among these pre-treatment technologies, thermal hydrolysis was the first applied since late 1970, and is recognized as one of the most common and successful pretreatment methods for its significant enhancement of AD performance (Li *et al.* 2017). Two main thermal hydrolysis processes are developed based on different applied temperatures: low temperature thermal hydrolysis applying moderate temperatures (normally under 100 °C) (Appels *et al.* 2010); and high temperature thermal hydrolysis with temperature of 100–210 °C (Neumann *et al.* 2016). Owing to the relative low applied temperature, it took several hours to solubilize organic matters in sludge by low temperature hydrolysis (Clement *et al.* 2007), while only 20–60 min was needed to achieve 12–80% chemical oxygen demand (COD) solubilization by high temperature treatment (Neumann *et al.* 2016). Hydrolysis temperature and hydrolysis time are two crucial variables for thermal hydrolysis. An improved temperature can significantly shorten pretreatment time; however, recalcitrant compounds may generate under temperatures over 170–190 °C (Carrere *et al.* 2010), which may further inhibit biogas production. Therefore, an optimum range of hydrolysis temperature and hydrolysis time is recommended for sludge pretreatment.

Steam explosion is a variation of high temperature thermal hydrolysis, which consists of the application of high temperature with high pressure steam in a reaction vessel, and a sudden release of the vapor pressure (called flashing). The sudden release of the pressure produces a strong shear effect on the sludge that further enhances the sludge disintegration after high temperature thermal treatment. Therefore, steam explosion could achieve better pretreatment performance than thermal hydrolysis under the same thermal treatment condition. Its enhancement performance for AD of WAS (Dereix *et al.* 2006) as well as pig manure (Ferreira *et al.* 2014), olive mill solid waste (Rincon *et al.* 2016), and rice straw (Zhou *et al.* 2016) has been reported. However, the effect of the two key operation parameters, hydrolysis temperature and hydrolysis time, of steam explosion on solubilization and AD of WAS was rarely studied (Perez-Elvira *et al.* 2015; Sapkaite *et al.* 2017). As steam explosion supplemented a mechanical disintegration step by flashing after thermal treatment, optimum ranges of operation variables for high temperature thermal hydrolysis can not be applied to steam explosion directly. Perez-Elvira *et al.* (2015) studied the relationship between the severity factor (logR₀) of steam explosion and sludge solubilization, and biochemical methane potential; however, the influence of each of the two key operation variables was not clarified. Sapkaite *et al.* (2017) investigated the influence of hydrolysis temperature and hydrolysis time on biochemical methane potential; however the impact of steam explosion on methane production rate was not analyzed. Besides, steam explosion influences physicochemical properties, which further influence followed treatment process. For example, particle size may influence the efficiency of sludge dewatering, and viscosity may also influence dewatering efficiency as well as the agitation power during digestion. However, the variation of physicochemical properties of sludge treated with steam explosion has not been investigated yet.

This study conducted sludge pretreatment by steam explosion under 12 operation conditions combined with different hydrolysis temperatures and times (Table 1). The

Table 1 | Operating parameters and severity factor of steam explosion adopted in this study

	TH ₁	TH ₂	TH ₃	TH ₄	TH ₅	TH ₆	TH ₇	TH ₈	TH ₉	TH ₁₀	TH ₁₁	TH ₁₂
T (°C)	151	151	151	164	164	164	179	179	179	198	198	198
t (min)	4	8	12	4	8	12	4	8	12	4	8	12
logR ₀	2.10	2.40	2.58	2.49	2.79	2.96	2.93	3.23	3.41	3.49	3.79	3.96

effect of steam explosion under different operation conditions on the main physicochemical properties as well as AD performance of WAS were revealed.

MATERIALS AND METHODS

Sludge

The substrate for steam explosion and digestion, WAS, was taken from a dewatered sludge tank of a local wastewater treatment plant (WWTP), in which the sludge was pre-dewatered by a belt press filter. The seed anaerobic sludge, which provided anaerobic microorganisms for digestion, was anaerobic granular sludge taken from an up-flow anaerobic sludge bed of another local WWTP in Wuxi city, China. The WAS had pH of 7.3, total solids (TS) concentration of 136 g/L, volatile solids (VS)/TS ratio of 53.67%, soluble chemical oxygen demand (SCOD) of 761.5 mg/L, soluble protein of 71.6 mg/L, soluble polysaccharide of 88.4 mg/L, ammonium nitrogen ($\text{NH}_4^+\text{-N}$) of 52.8 mg/L, and total phosphorus (TP) of 8.2 mg/L. The seed anaerobic sludge had pH of 7.5 mg/L, TS of 110 mg/L, VS/TS ratio of 68.52%, and $\text{NH}_4^+\text{-N}$ of 526.6 mg/L.

Steam explosion device and operation parameters

A steam-explosion machine (QBS-80, Zhengdao, China) with heating power of 8 kW, maximum vapor pressure of 3.2 MPa, cylinder capacity of 400 mL, was used in this study. A 200 g WAS was treated in each steam explosion batch. Total 12 sets of steam explosion parameters, which covered four different hydrolysis temperatures and three different hydrolysis times, were applied. The detailed steam explosion parameters are shown in Table 1. The severity factor, $\log R_0$, of thermal hydrolysis was calculated by Equation (1) (Ferreira *et al.* 2014).

$$\log R_0 = \log \left(t \times \exp \left(\frac{T - 100}{14.75} \right) \right) \quad (1)$$

T is the pretreatment temperature, °C; t is the pretreatment time, min.

Sludge AD

AD was carried out in 1 L glass conical flasks containing 400 mL steam explosion pretreated WAS as substrate and

80 mL seed anaerobic sludge providing anaerobic microorganisms. After sludge was added, the headspace of the flask was filled with N_2 gas for 5 min to eliminate O_2 . Then, the flask was sealed with a rubber stopper, in which a glass tube was inserted to collect biogas. 400 mL un-pretreated WAS digested with 80 mL seed anaerobic sludge was conducted as the experimental control (EC). Meanwhile, 80 mL seed anaerobic sludge digested with no WAS feeding was conducted as the blank control (BC). All the digestion experiments were implemented in an oscillating water bath under 35 °C for 30 days. The pH, SCOD, and $\text{NH}_4^+\text{-N}$ in the digestion liquid were determined daily.

Analytical methods

Conventional indices, including TV, VS, $\text{NH}_4^+\text{-N}$, TP, SCOD, and pH were analyzed according to the standard methods. Particle size distribution was measured by a laser particle size distribution instrument (BT-2003, Bettersize, China). Capillary suction time (CST) was tested by a Type 304M CST analyzer. Viscosity was determined by a rheometer (LVDV-3T, Brookfield, MA). The soluble phase was obtained by centrifugation at 10,000 rpm for 5 min, and filtrated with a 0.45 μm membrane. The concentrations of polysaccharide and protein were measured by the phenol-sulfuric acid method (Dubois *et al.* 2002) and the Coomassie brilliant blue staining method (Bradford 1976), respectively. The solubilization of the WAS treated with steam explosion was assessed with solubilization ratio (SR), which was calculated by Equation (2).

$$\text{SR} = \frac{\text{VS}_0 - \text{VS}_t}{\text{VS}_0} \times 100\% \quad (2)$$

VS_0 is the initial VS of the WAS before steam explosion pretreatment; VS_t is the VS of the WAS after steam explosion pretreatment.

The volume of produced biogas was measured by displacement of saturated aqueous NaCl in a graduated measuring cylinder (Abouelenien *et al.* 2009). The volume of cumulative biogas from sludge digestion systems was amended with that from BC, which was the biogas produced by endogenous respiration of the seed anaerobic sludge. The specific biogas production rate was obtained by normalizing the volume of cumulative biogas with initial VS fed for AD before steam explosion (VS_{fed}). Therefore, the effect of steam explosion operation condition on the performance of sludge AD could be investigated by comparing specific

biogas production rate. Methane content in biogas was determined by a GC (GC9790II, Fuli, China).

Modelling

The biogas production curves were fitted to three models in order to obtain the kinetic parameters. The three considered biogas production models were modified Gompertz (MG) (Nopharatana *et al.* 2007), transference function (TF) (Donoso-Bravo *et al.* 2011), and logistic function (LF) (Donoso-Bravo *et al.* 2010), shown as Equations (3)–(5), respectively.

$$B = P \times \exp \left\{ - \exp \left[\frac{R_m \times e}{P} (\lambda - t) + 1 \right] \right\} \quad (3)$$

$$B = P \times \left[1 - \exp \left(\frac{-R_m(t - \lambda)}{P} \right) \right] \quad (4)$$

$$B = \frac{P}{1 + \exp \left[\frac{4R_m(\lambda - t)}{P} + 2 \right]} \quad (5)$$

In the models, B is the cumulative biogas production (mL), P is biogas production potential (mL), R_m is the maximum biogas production rate (mL/d), λ is the duration of the lag phase (d), and t is the duration of the digestion at which cumulative biogas production, B , is calculated (d). Adjusted R^2 (adj. R^2) was calculated to evaluate the accuracy of each model. The R_m obtained from the most accurate model was used to compare the maximum biogas production rate of the digestion of pretreated WAS under different steam explosion condition.

RESULTS AND DISCUSSION

Changes in physicochemical properties of the sludge

Particle size distribution, CST, and viscosity of the sludge before and after steam explosion were measured. As shown in Figure 1(a), sludge particle size was decreased by steam explosion pretreatment. The decrease was generally enlarged with hydrolysis temperature improvement and hydrolysis time extension. The median diameter (D50) was decreased from 61.56 μm in raw sludge to 28.9 μm in that treated under 198° C for 8 min. The decreased particle size was also observed during hydrothermal (Park *et al.* 2017) and other pretreatment (Zhang *et al.* 2016), which was probably owing to flocculation disintegration caused by

solubilization of extracellular polymeric substances (EPS) and lysed cells. However, when the hydrolysis time was extended to 12 min under 198° C, the particle size of the sludge rebounded to D50 of 58.91 μm , which was very close to that of the raw sludge.

CST and viscosity were gradually increased with the improvement of steam explosion severity, e.g. increased hydrolysis temperature and prolonged hydrolysis time (shown in Figure 1(b)). As EPS often positively influence CST (Neyens *et al.* 2004) and viscosity (Li & Yang 2007), the significantly increased CST and viscosity, from 17.1 s and 201.9 cP in the raw sludge to 690.0 s and 520.8 cP in the sludge treated under 198° C for 8 min, indicated a high possibility of enhanced extracellular organic matter in the sludge with steam explosion pretreatment. The increased CST indicated that the dewaterability of the sludge was deteriorated, which occurs frequently after pretreatment due to the destruction of sludge flocs and the release of EPS (Zhu *et al.* 2015; Liu *et al.* 2017). The deterioration of sludge dewaterability caused by steam explosion was lower than that caused by thermal alkaline hydrolysis, which could increase CST of the sludge from 40–50 s to about 2,500 s under 90° C, pH 12.0 of 3 h (Liu *et al.* 2017). The less deterioration of sludge dewaterability could be one of the advantages of steam explosion for sludge pretreatment.

The CST and viscosity of the sludge treated under 198° C 12 min were 707.2 s and 505.2 cP respectively, similar to that of the sludge treated under 198° C for 8 min and much higher than that of the raw sludge. This indicated that a large amount of intracellular organic matters may also released under 198° C for 12 min. The increased sludge particle size when hydrolysis time is prolonged from 8 min to 12 min under 198° C was probably attributed to the re-aggregation of the sludge after disintegration and solubilization under high pretreatment severity.

Solubilization of organic matters in steam exploded sludge

The SCOD, soluble polysaccharide, soluble protein, NH_4^+-N , and TP concentration in the liquid phase as well as the SR was determined to evaluate the solubilization of the sludge treated by steam explosion. As shown in Figure 2(a), the SR of the sludge treated by steam explosion ranged from 23.9–41.3%, indicated a good solubilization of steam explosion treated sludge. The highest SR appeared in the sludge treated with 198° C for 12 min, while the lowest SR showed in the sludge treated with 151° C for 4 min. The SR seems to be improved with the increasing of hydrolysis temperature and

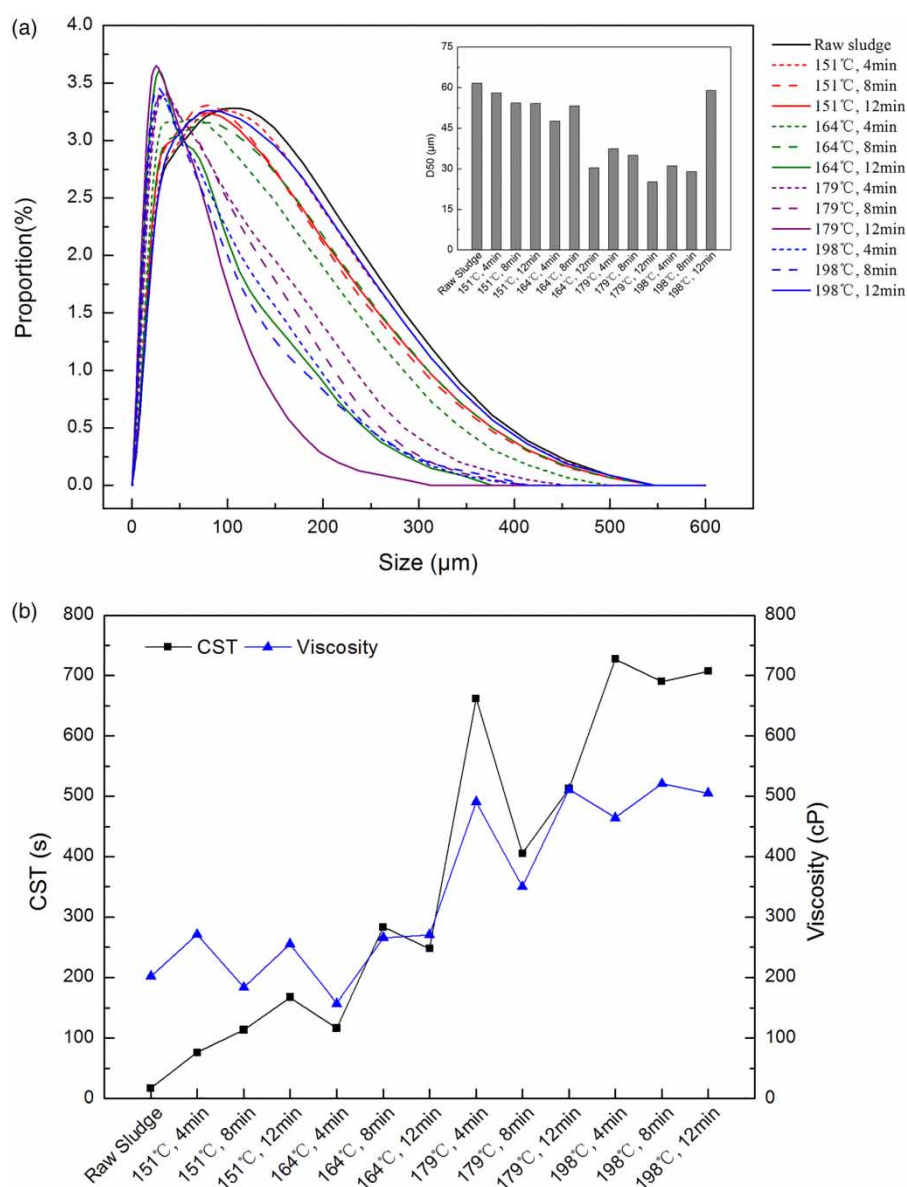


Figure 1 | Changes in physicochemical properties of the sludge. (a) Particle size distribution; (b) CST and viscosity.

extending of hydrolysis time. Consistently, the SCOD in the sludge increased from 761 mg/L to 6,396–9,718 mg/L with the pretreatment of steam explosion, and the soluble polysaccharide and protein were improved from 88 mg/L and 71 mg/L to 1,457 mg/L and 866 mg/L, respectively. Both polysaccharide and protein showed a good linear correlation with SCOD, with Pearson r of 0.9553 and 0.9379 respectively (shown in Figure S1, available with the online version of this paper). However, polysaccharide increased faster than protein with SCOD increasing, which indicated that the intracellular polysaccharide released more and faster than protein during steam explosion pretreatment. A high

proportion of protein in the substrate will result in a high concentration of ammonia, which may substantially influence AD performance (Chen *et al.* 2008). The more released polysaccharide with steam explosion pretreatment could increase the C/N ratio of the available substrate in the sludge, and benefit biogas production.

$\text{NH}_4^+\text{-N}$ and TP in the liquid phase were also increased significantly after steam explosion, which ranged 425–1,032 mg/L and 41–98 mg/L, respectively (Figure 2(b)). There was a substantial increase of $\text{NH}_4^+\text{-N}$ concentration when the hydrolysis temperature increased from 164°C to 179°C, which was consistent with the finding by Wilson

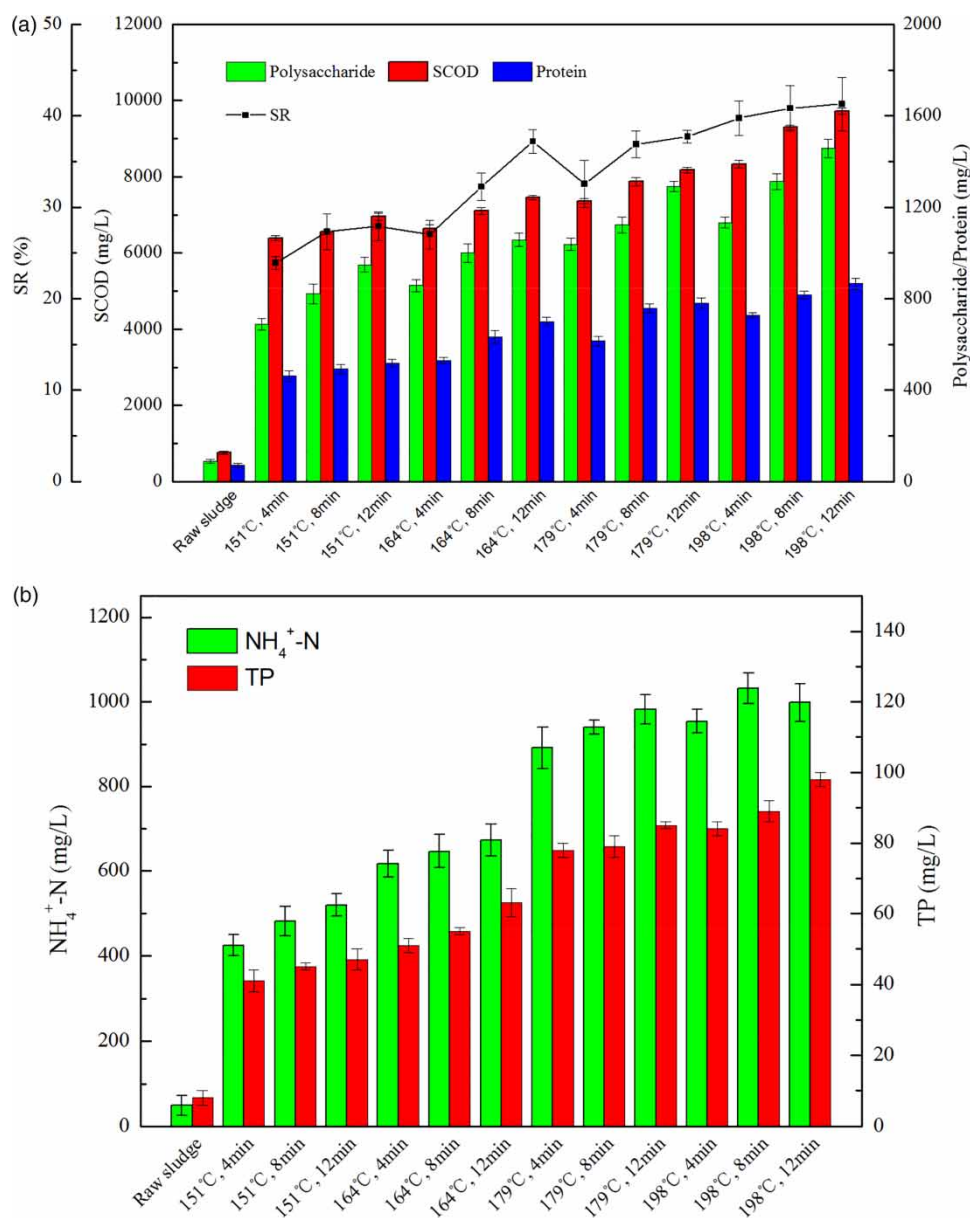


Figure 2 | Solubilization of organic matters in steam exploded sludge. (a) soluble COD, soluble polysaccharide, soluble protein, and SR; (b) soluble NH_4^+-N and TP of steam explosion pretreated sludge.

& Novak (2009), e.g. the release of NH_4^+-N was significantly improved when hydrolysis temperature was over 170 °C. The TP concentration was gradually increased with hydrolysis time extension under each treatment temperature. The variation of NH_4^+-N concentration was consistent with TP under temperatures of 151 °C, 164 °C, and 179 °C. However, NH_4^+-N concentration decreased with hydrolysis time prolonged from 8 min to 12 min under 198 °C. The decreased soluble NH_4^+-N concentration in steam explosion treated sludge was also found when hydrolysis temperature increased from 180 °C to 260 °C (Dereix *et al.* 2006);

however the possible reason was not discussed. As melanoidins could probably generate when the hydrolysis temperature was relatively high of 180 °C via Maillard reaction (Wilson & Novak 2009), which polymerized amino acids and saccharides, the decreased NH_4^+-N could probably be attributed to melanoidins generation.

According to the SR of the WAS and concentration improvement of the SCOD, soluble polysaccharide, soluble polysaccharide, NH_4^+-N , and TP, the enhancement of sludge solubilization by steam explosion treatment was revealed. Wang *et al.* (2009) also found the effective release

of polysaccharide and other biodegradable compounds from steam explosion treated straw, demonstrated the good pretreatment performance of steam explosion.

The relationship of steam explosion and organics solubilization

The $\log R_0$ is an effective factor to represent the severity of steam explosion, which directly influences sludge pretreatment performance. The relationships between $\log R_0$ and SR, and SCOD were evaluated to investigate the effect of steam explosion severity on the sludge solubilization. As shown in Figure 3, both SR and SCOD showed significant linear correlations with $\log R_0$, indicated that a higher steam explosion severity could result in a better solubilization of sludge. Hydrolysis temperature and hydrolysis time are the

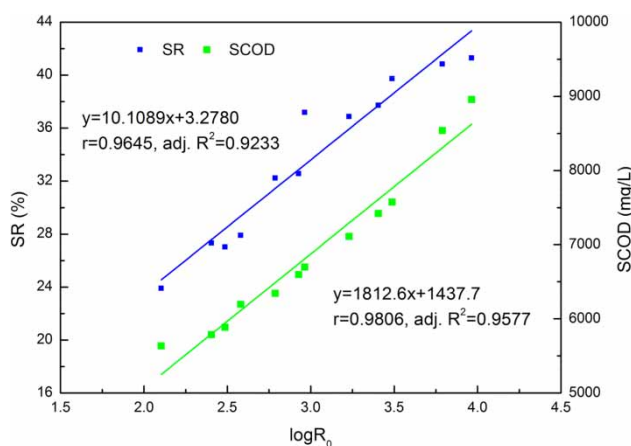


Figure 3 | The correlation between SR, SCOD and $\log R_0$.

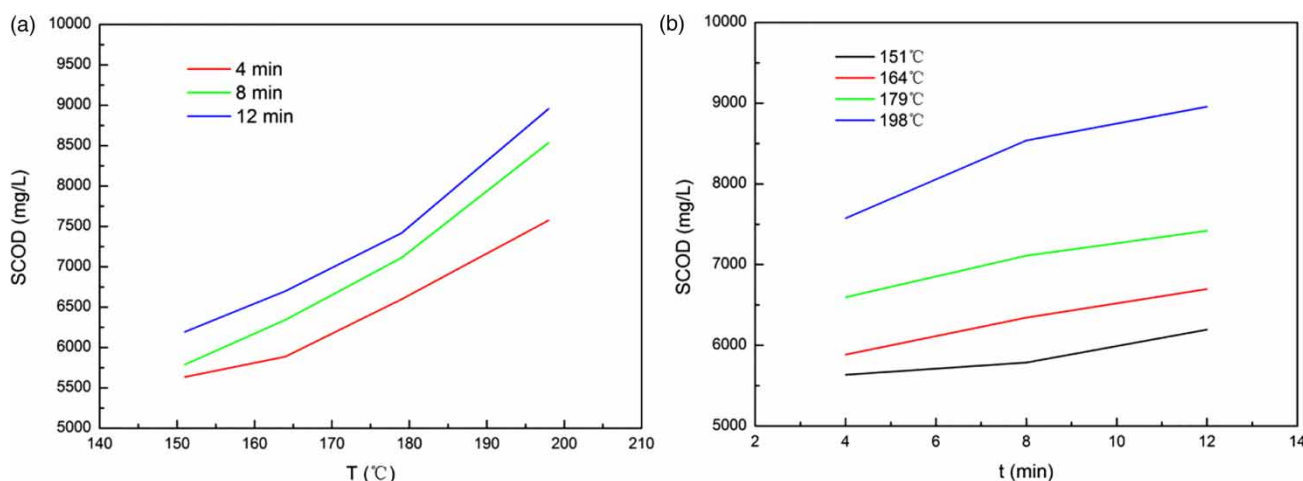


Figure 4 | Effect of (a) hydrolysis temperature and (b) hydrolysis time on sludge solubilization.

two parameters determining steam explosion treatment severity. With one of the two factors kept constant, increase of the other improves the steam explosion severity, thus may enhance the solubilization of the treated sludge. Consequently, the SCOD concentration in the WAS treated with higher hydrolysis temperature and longer hydrolysis time was generally higher (shown in Figure 4). However, under different hydrolysis time, the enhanced magnitude of sludge solubilization by increased hydrolysis temperature was not consistent. As shown in Figure 4(a), when hydrolysis time was relatively short at 4 min, the slope of the SCOD curve from temperature 151 to 164 °C was significantly lower than the curve from temperature 164 to 198 °C. It indicated that the specific solubilization enhancement rate by increasing temperature in the range of 151–164 °C was less than that in the range of 164–198 °C. Similarly, when hydrolysis time was 8 min and 12 min, the specific solubilization enhancement rate by increasing temperature in relatively low temperature range (151–179 °C) was slightly lower than in the higher temperature range (179–198 °C). It revealed that increasing hydrolysis temperature in the relatively high temperature range could improve more sludge solubilization, which was probably owing to higher hydrolysis rate under high temperature.

In addition, different enhancement of sludge solubilization by increased hydrolysis time under different hydrolysis temperature was also revealed (shown in Figure 3(b)). The slope of SCOD curve from 8–12 min of 151 °C was higher than that from 4–8 min, indicating a better solubilization enhancement by extending hydrolysis time in the longer hydrolysis time range. However, the slope of the two fragments of SCOD curve of 164 °C was similar; and the curves from

4–8 min of 179 °C and 198 °C were steeper than their corresponding fragments from 8–12 min, which was contrary to that of 151 °C. This phenomenon revealed that when hydrolysis temperature was relatively low at 151 °C, a longer hydrolysis time was recommended for effectively increasing the sludge solubilization; while under a higher hydrolysis temperature of 198 °C, the hydrolysis time could be shorter. Xue *et al.* (2015) revealed that a longer hydrolysis time (24 h) was needed to effectively hydrolyze sludge by low-temperature thermal hydrolysis (60–90 °C), while only 180 min was required to achieve a good pretreatment performance by high-temperature thermal hydrolysis (120–180 °C). Higher temperature significantly increases the sludge solubilization and organics release. The reported hydrolysis time for high-temperature thermal hydrolysis (20–60 min) was much shorter than that for lower-temperature thermal hydrolysis (up to 7 days) (Neumann *et al.* 2016). Steam explosion has the advantages of high-temperature thermal hydrolysis, and developed a better means, flashing, for sludge disintegration. Therefore, steam explosion could achieve an excellent hydrolysis performance within several minutes (Zhou *et al.* 2016), much shorter than that for high-temperature thermal hydrolysis.

Biogas production from steam explosion pretreated sludge

The biogas production by AD from steam explosion pretreated sludge was investigated. The cumulative biogas amount is shown in Figure 5. The amount of produced

biogas from steam explosion pretreatment sludge (1,651–2,930 mL) was significantly more than that from un-pretreated sludge (537 mL) after 30 days' digestion.

To further compare the effect of steam explosion operation condition on performance of sludge AD, specific biogas production rate was calculated by normalizing the volume of cumulative biogas with VS_{fed} . The specific biogas production rate was improved from 22.4 mL/g VS_{fed} to 68.8–122.1 mL/g VS_{fed} by steam explosion pretreatment. Moreover, the biogas was produced faster from steam explosion pretreated sludge than the untreated sludge. After pretreatment, biogas generated fastest at the beginning of the digestion, and gradually slowed down as the digestion continued. The proportion of the biogas produced in the first 6 days was 43.5–62.7% in the pretreated sludge digestion system, which was much higher than 27.0% in the EC. The improved biogas amount and the accelerated biogas production demonstrated the excellent pretreatment performance of steam explosion. Consistently, the biogas production was significantly accelerated from pig manure by steam explosion treatment under 170 °C for 30 min, the specific biogas production rate was two times more than that of the un-pretreated control (Ferreira *et al.* 2014). Besides biogas production, methane content in the biogas was also improved from 18.3% in the EC to around 50% in the pretreated sludge digestion system. The relatively low specific biogas production rate (22.4–122.1 mL/g VS_{fed}) in this study was attributed to the low inoculation rate of seed anaerobic sludge (16.7%). High inoculation

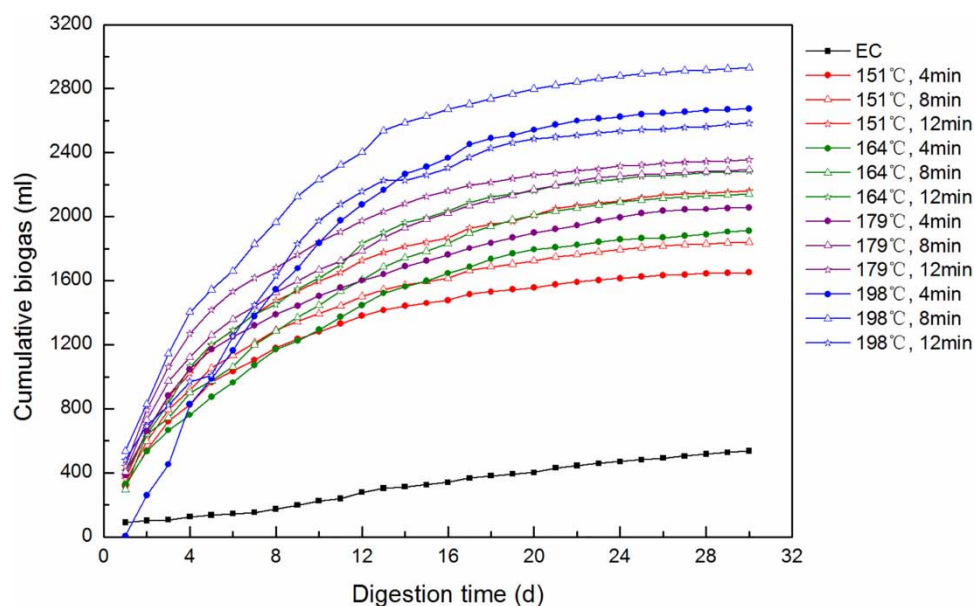


Figure 5 | Cumulative biogas during AD of steam exploded sludge.

rate of seed anaerobic sludge could significantly increase the biogas production rate of AD (Liu *et al.* 2009).

The biogas production curves were fitted to three models in order to obtain the kinetic parameters. As shown in Table S1 (available with the online version of this paper), the average adj. R^2 of model TF fitting for all the biogas production curves was 0.9817, which was higher than that of model MG (average adj. $R^2 = 0.9487$) and model LF (average adj. $R^2 = 0.9371$). It indicated that model TF was the most accurate one for biogas production modelling in this study. Therefore, R_m calculated by model TF (shown in Table S1) was used to analyze the influence of steam explosion on the maximum biogas production rate. It was found that the R_m significantly increased from 26.3 mL/d in the EC to 225.7–399.1 mL/d in the digestion system of pretreated sludge, indicating the improved maximum biogas production rate along with the specific biogas production rate by steam explosion.

The relationship of steam explosion and biogas production improvement

The effect of steam explosion variables on biogas production improvement was investigated. It is revealed in Figure 5 that cumulative biogas production was improved with hydrolysis time extended under the same hydrolysis temperatures of 151 °C, 164 °C, and 179 °C, but not 198 °C. The relationship between improved biogas production and hydrolysis temperature showed the same phenomenon (shown in Figure 6(a)). Under 151 °C, the improved biogas production was significantly enhanced with extended hydrolysis time. While under 164 °C and 179 °C, the improved biogas production was also enhanced with extended hydrolysis time, though the enhancement from 8 min to 12 min was slight. However, when the hydrolysis time was prolonged from 8 min to 12 min under 198 °C, the improvement of biogas production was reduced, though the solubilization of the sludge was the best (Figure 2(a)). It indicated that high sludge solubilization caused by steam explosion is not bound to a good biogas production if the sludge is pretreated under a high temperature for an overlong time. Consistent with biogas production, the R_m was improved by prolonging hydrolysis time under hydrolysis temperatures of 151 °C, 164 °C, and 179 °C; however, the R_m was significantly decreased when the hydrolysis time was extended from 8 min to 12 min under hydrolysis temperature of 198 °C. From the relationship between hydrolysis temperature and improved biogas production (Figure 6(c)), it can be seen that the enhancement of biogas production with hydrolysis temperature improvement under hydrolysis time of 12 min

was less significant than that under hydrolysis times of 4 min and 8 min. Similarly, when hydrolysis temperature increased to 198 °C, the R_m was significantly enhanced with hydrolysis times of 4 min and 8 min; however, it decreased under hydrolysis time of 12 min (shown in Figure 6(d)).

The relationship between improved biogas production, R_m and $\log R_0$ was evaluated and is shown in Figure 6(e) and 6(f) respectively. Generally, both biogas production and R_m showed improvement with increased $\log R_0$. However, both biogas production and R_m significantly decreased under the highest $\log R_0$ in this study ($\log R_0 = 3.96$). If the data at $\log R_0$ of 3.96 is excluded, biogas production and R_m showed better linear correlations with $\log R_0$, with Pearson r of 0.9492 and 0.9171 respectively. Compared to the correlation between sludge solubilization and $\log R_0$ (Figure 3), it is revealed that increasing $\log R_0$ generally could enhance both sludge solubilization and biogas production. However, when $\log R_0$ was 3.96, though a better sludge solubilization was achieved, the biogas production significantly decreased compared to $\log R_0$ of 3.79. Similarly, Ferreira *et al.* (2014) found that the methane productivity and R_m under $\log R_0$ of 3.83 was substantially reduced compared to that under $\log R_0$ of 3.53, when applying steam explosion to pig manure pretreatment. Perez-Elvira *et al.* (2015) revealed that the R_m of the sludge pretreated under $\log R_0$ of 4.1 and 3.8 was also significantly decreased compared to that under $\log R_0$ of 3.1. As shown in Figure S2 (available with the online version of this paper), the residual SCOD in the sludge after digestion was gradually increased from 612 mg/L in the EC to 1,723 mg/L in the sludge treated under 198 °C for 8 min. A linear correlation was revealed between SCOD and $\log R_0$, when the $\log R_0$ was less than 3.80. However, the residual SCOD substantially increased to 3,245 mg/L under $\log R_0$ of 3.96. Consistent with the relatively low concentration of $\text{NH}_4^+\text{-N}$ in the steam exploded sludge (Figure 2(b)), the increased SCOD in the sludge after digestion also indicated that more refractory organics like melanoidins were probably generated under high $\log R_0$ of 3.96, which resulted in a relatively low biogas production. Therefore, it was inappropriate to extend hydrolysis time as long as 12 min under hydrolysis temperature of 198 °C. A severity of $\log R_0$ lower than 3.96 was recommended in steam explosion for sludge pretreatment.

Effect of steam explosion pretreatment on pH and $\text{NH}_4^+\text{-N}$ during sludge digestion

The pH and $\text{NH}_4^+\text{-N}$ concentration are two important factors which may greatly influence the performance of AD.

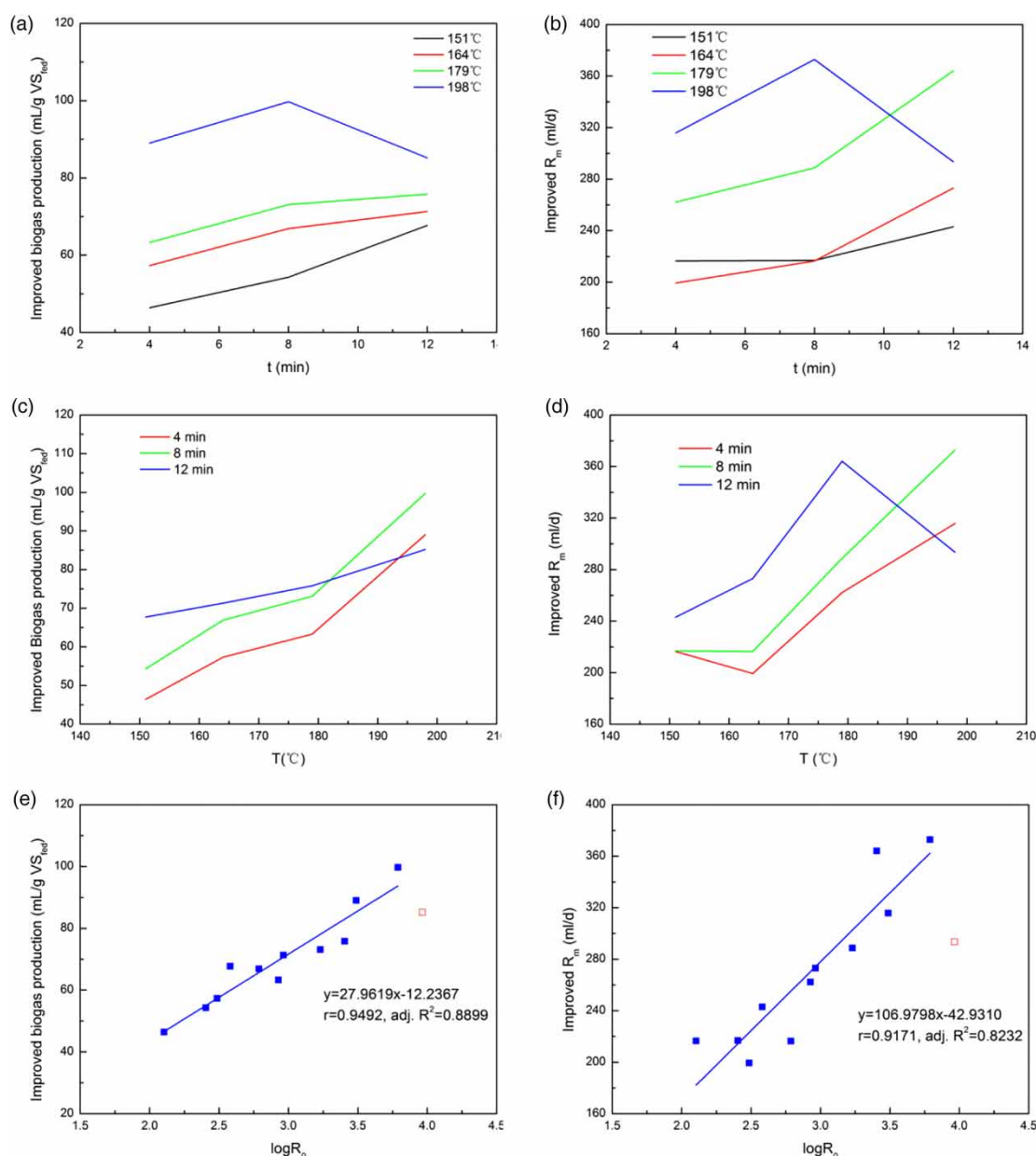


Figure 6 | Relationship between improved biogas production and (a) hydrolysis time, (c) hydrolysis temperature, (e) severity factor; and between improved R_m and (b) hydrolysis time, (d) hydrolysis temperature, (f) severity factor.

If pH and $\text{NH}_4^+\text{-N}$ concentration deviate from the optimum range, the activity of anaerobic microorganisms will be inhibited and the digestion may fail. Therefore, the effect of steam explosion on pH and $\text{NH}_4^+\text{-N}$ was also investigated.

The variation of pH during sludge AD is shown in Figure S3 (available with the online version of this paper). In EC, pH decreased from 6.79 to 6.71 in the first two days of the digestion. The decrease of pH may be owing to volatile fatty acid (VFA) accumulation in the digestion system.

Subsequently, the pH in EC increased to 7.27 on day 5, and fluctuated between 7.12–7.38. In the pretreated sludge digestion systems, the pH directly increased from 6.61–6.92 to 7.18–7.51 in the first two days of digestion, then kept relatively steady in 7.34–7.69. Steam explosion pretreatment accelerated biogas production, avoided pH reduction caused by VFA accumulation at the initial stage of digestion, and increased the final pH to 7.43–7.72, which was well within the optimum pH range for methane production by AD.

A high $\text{NH}_4^+\text{-N}$ concentration could induce a high concentration of free ammonia nitrogen (FAN), which has been suggested to be the main cause of inhibition since it is freely membrane permeable. The inhibition concentration of FAN could be dozens to hundreds of mg/L in AD systems with different substrates, microorganisms, digestion temperature, etc. (Chen et al. 2008; Kim et al. 2011; Hidaka et al. 2013). During digestion, the initial $\text{NH}_4^+\text{-N}$ concentration in the pretreated sludge was 570–1,087 mg/L higher than the EC, owing to the enhanced release of intracellular organics by steam explosion. The $\text{NH}_4^+\text{-N}$ concentration in the EC rapidly increased in the first two days of digestion, then slowly increased during the whole digestion period (shown in Figure S4, available with the online version of this paper). The $\text{NH}_4^+\text{-N}$ concentration in the pretreated sludge digestion system gradually increased in the first 15 days, then kept steady in the following digestion period. As shown in Figure S4, maximum $\text{NH}_4^+\text{-N}$ concentration during digestion was increased by 459–1,064 mg/L in the steam explosion pretreated sludge digestion systems comparing to that in the EC. The FAN during AD was calculated according to Angelidaki & Ahring (1993), and was found at 3.43–72.25 mg/L in the steam explosion pretreated sludge systems higher than that in the un-pretreated ones (0.33–9.66 mg/L). Fortunately, the highest $\text{NH}_4^+\text{-N}$ concentration and FAN concentration in each pretreated sludge digestion system was 938–1,543 mg/L and 37.22–72.25 mg/L, respectively, which was considered as a safe concentration for biogas production (Chen et al. 2008; Duan et al. 2012).

CONCLUSIONS

The influence of key operation parameters of steam explosion on physicochemical properties and AD of WAS was investigated. Steam explosion decreased the particle size and increased the CST and viscosity of WAS. The improvement of sludge solubilization, biogas production, and maximum biogas production rate was obtained under all the operation conditions of steam explosion. Better sludge solubilization was obtained under the largest steam explosion severity of 3.96; however, the highest biogas production was achieved under $\log R_0$ of 3.79. The results suggest that 198° C and 8 min ($\log R_0 = 3.79$) are the optimum operation parameters of steam explosion for WAS pretreatment, which could improve biogas production by 99.7 mL/g VS_{fed} . The pH and $\text{NH}_4^+\text{-N}$ during sludge AD was increased by steam explosion pretreatment; however, no inhibition on biogas production was observed.

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CONFLICTS OF INTEREST

None.

REFERENCES

- Abouelenien, F., Kitamura, Y., Nishio, N. & Nakashimada, Y. 2009 [Dry anaerobic ammonia-methane production from chicken manure](#). *Applied Microbiology and Biotechnology* **82** (4), 757–764.
- Angelidaki, I. & Ahring, B. 1993 [Thermophilic anaerobic digestion of livestock waste: the effect of ammonia](#). *Applied Microbiology and Biotechnology* **38**, 560–564.
- Appels, L., Degreve, J., Bruggen, B. V., Impe, J. V. & Dewil, R. 2010 [Influence of low temperature thermal pre-treatment on sludge solubilisation, heavy metal release and anaerobic digestion](#). *Bioresource Technology* **101**, 5743–5748.
- Bougrier, C., Delgenes, J. P. & Carrere, H. 2007 [Impacts of thermal pre-treatments on the semi-continuous anaerobic digestion of waste activated sludge](#). *Biochemical Engineering Journal* **34** (1), 20–27.
- Bradford, M. M. 1976 [A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein-dye binding](#). *Analytical Biochemistry* **72** (1), 248–254.
- Carrere, H., Dumas, C., Battimelli, A., Batstone, D. J., Delgenes, J. P., Steyer, J. P. & Ferrer, I. 2010 [Pretreatment methods to improve sludge anaerobic degradability: a review](#). *Journal of Hazardous Materials* **183** (1–3), 1–15.
- Chen, Y., Cheng, J. J. & Creamer, K. S. 2008 [Inhibition of anaerobic digestion process: a review](#). *Bioresource Technology* **99** (10), 4044–4064.
- Climent, M., Ferrer, I., del Mar Baeza, M., Artola, A., Vazquez, F. & Font, X. 2007 [Effects of thermal and mechanical pretreatments of secondary sludge on biogas production under thermophilic conditions](#). *Chemical Engineering Journal* **133** (1–3), 335–342.
- Dereix, M., Parker, W. & Kennedy, K. 2006 [Steam-explosion pretreatment for enhancing anaerobic digestion of municipal wastewater sludge](#). *Water Environment Research* **78** (5), 474–485.
- Devlin, D. C., Esteves, S. R. R., Dinsdale, R. M. & Guwy, A. J. 2011 [The effect of acid pretreatment on the anaerobic digestion and dewatering of waste activated sludge](#). *Bioresource Technology* **102** (5), 4076–4082.
- Donoso-Bravo, A., Perez-Elvira, S. I. & Fdz-Polanco, F. 2010 [Application of simplified models for anaerobic](#)

- biodegradability tests. Evaluation of pre-treatment processes. *Chemical Engineering Journal* **160** (2), 607–614.
- Donoso-Bravo, A., Perez-Elvira, S., Aymerich, E. & Fdz-Polanco, F. 2011 Assessment of the influence of thermal pre-treatment time on the macromolecular composition and anaerobic biodegradability of sewage sludge. *Bioresource Technology* **102** (2), 660–666.
- Duan, N., Dong, B., Wu, B. & Dai, X. 2012 High-solid anaerobic digestion of sewage sludge under mesophilic conditions: feasibility study. *Bioresource Technology* **104**, 150–156.
- Dubois, M., Gilles, K. A., Hamilton, J. K., Rebers, P. A. & Smith, F. 2002 Colorimetric method for determination of sugars and related substances. *Analytical Chemistry* **28** (3), 350–356.
- Ferreira, L. C., Souza, T. S. O., Fdz-Polanco, F. & Perez-Elvira, S. I. 2014 Thermal steam explosion pretreatment to enhance anaerobic biodegradability of the solid fraction of pig manure. *Bioresource Technology* **152**, 393–398.
- Gianico, A., Braguglia, C. M., Cesarini, R. & Mininni, G. 2013 Reduced temperature hydrolysis at 134 degrees C before thermophilic anaerobic digestion of waste activated sludge at increasing organic load. *Bioresource Technology* **143**, 96–103.
- Hidaka, T., Wang, F., Togari, T., Uchida, T. & Suzuki, Y. 2013 Comparative performance of mesophilic and thermophilic anaerobic digestion for high-solid sewage sludge. *Bioresource Technology* **149**, 177–183.
- Kim, D. & Oh, S. 2011 Continuous high-solids anaerobic co-digestion of organic solid wastes under mesophilic conditions. *Waste Management* **31** (9–10), 1943–1948.
- Lee, L.-J., Lee, Y.-S. & Han, G.-B. 2017 Effect of two-step thermolysis on the enhancing solubilization and anaerobic biodegradability of excess waste sludge. *Chemical Engineering Journal* **317**, 742–750.
- Li, X. Y. & Yang, S. F. 2007 Influence of loosely bound extracellular polymeric substances (EPS) on the flocculation, sedimentation and dewaterability of activated sludge. *Water Research* **41** (5), 1022–1030.
- Li, W., Guo, J., Cheng, H., Wang, W. & Dong, R. 2017 Two-phase anaerobic digestion of municipal solid wastes enhanced by hydrothermal pretreatment: viability, performance and microbial community evaluation. *Applied Energy* **189**, 613–622.
- Lin, Y., Wang, D., Wu, S. & Wang, C. 2009 Alkali pretreatment enhances biogas production in the anaerobic digestion of pulp and paper sludge. *Journal of Hazardous Materials* **170** (1), 366–373.
- Liu, G., Zhang, R., El-Mashad, H. M. & Dong, R. 2009 Effect of feed to inoculum ratios on biogas yields of food and green wastes. *Bioresource Technology* **100** (21), 5103–5108.
- Liu, H., Wang, Y., Wang, L., Yu, T., Fu, B. & Liu, H. 2017 Stepwise hydrolysis to improve carbon releasing efficiency from sludge. *Water Research* **119**, 225–233.
- Neumann, P., Pesante, S., Venegas, M. & Vidal, G. 2016 Developments in pre-treatment methods to improve anaerobic digestion of sewage sludge. *Reviews in Environmental Science and Bio-Technology* **15** (2), 173–211.
- Neyens, E., Baeyens, J., Dewil, R. & De heyder, B. 2004 Advanced sludge treatment affects extracellular polymeric substances to improve activated sludge dewatering. *Journal of Hazardous Materials* **106** (2–3), 83–92.
- Nopharatana, A., Pullammanappalli, P. C. & Clarke, W. P. 2007 Kinetics and dynamic modelling of batch anaerobic digestion of municipal solid waste in a stirred reactor. *Waste Management* **27** (5), 595–603.
- Park, S., Yoon, Y.-M., Han, S. K., Kim, D. & Kim, H. 2017 Effect of hydrothermal pre-treatment (HTP) on poultry slaughterhouse waste (PSW) sludge for the enhancement of the solubilization, physical properties, and biogas production through anaerobic digestion. *Waste Management (New York, N.Y.)* **64**, 327–332.
- Perez-Elvira, S. I., Sapkaite, I. & Fdz-Polanco, F. 2015 Evaluation of thermal steam-explosion key operation factors to optimize biogas production from biological sludge. *Water Science and Technology* **72** (6), 937–945.
- Pilli, S., More, T. T., Yan, S., Tyagi, R. D. & Surampalli, R. Y. 2016 Fenton pre-treatment of secondary sludge to enhance anaerobic digestion: energy balance and greenhouse gas emissions. *Chemical Engineering Journal* **283**, 285–292.
- Rincon, B., Rodriguez-Gutierrez, G., Bujalance, L., Fernandez-Bolanos, J. & Borja, R. 2016 Influence of a steam-explosion pre-treatment on the methane yield and kinetics of anaerobic digestion of two-phase olive mil solid waste or alperujo. *Process Safety and Environmental Protection* **102**, 361–369.
- Sapkaite, I., Barrado, E., Fdz-Polanco, F. & Perez-Elvira, S. I. 2017 Optimization of a thermal hydrolysis process for sludge pre-treatment. *Journal of Environmental Management* **192**, 25–30.
- Wang, G., Gavala, H. N., Skiadas, I. V. & Ahring, B. K. 2009 Wet explosion of wheat straw and codigestion with swine manure: effect on the methane productivity. *Waste Management* **29** (11), 2830–2835.
- Wilson, C. A. & Novak, J. T. 2009 Hydrolysis of macromolecular components of primary and secondary wastewater sludge by thermal hydrolytic pretreatment. *Water Research* **43** (18), 4489–4498.
- Xue, Y., Liu, H., Chen, S., Dichtl, N., Dai, X. & Li, N. 2015 Effects of thermal hydrolysis on organic matter solubilization and anaerobic digestion of high solid sludge. *Chemical Engineering Journal* **264**, 174–180.
- Yin, Y., Liu, Y.-J., Meng, S.-J., Kiran, E. U. & Liu, Y. 2016 Enzymatic pretreatment of activated sludge, food waste and their mixture for enhanced bioenergy recovery and waste volume reduction via anaerobic digestion. *Applied Energy* **179**, 1131–1137.
- Zhang, J., Zhang, J., Tian, Y., Li, N., Kong, L., Sun, L., Yu, M. & Zuo, W. 2016 Changes of physicochemical properties of sewage sludge during ozonation treatment: correlation to sludge dewaterability. *Chemical Engineering Journal* **301**, 238–248.
- Zhou, J., Yan, B. H., Wang, Y., Yong, X. Y., Yang, Z. H., Jia, H. H., Jiang, M. & Wei, P. 2016 Effect of steam explosion pretreatment on the anaerobic digestion of rice straw. *RSC Advances* **6** (91), 88417–88425.
- Zhu, Y. F., Liu, H. B., Liu, H., Huang, S., Ma, H. J. & Tian, Y. 2015 Filtration characteristics of anaerobic fermented sewage sludge for fatty acids production. *Separation and Purification Technology* **142**, 8–13.