

Contents lists available at ScienceDirect

Bioresource Technology



journal homepage: www.elsevier.com/locate/biortech

Carbon dioxide sequestration and methane production promotion by wollastonite in sludge anaerobic digestion



Yan Zhang^{a,b,c}, Lihui Zhang^a, He Liu^{a,b,c,*}, Linlin Gong^a, Qianqian Jiang^a, Hongbo Liu^{a,b,c}, Bo Fu^{a,b,c}

^a School of Environment and Civil Engineering, Jiangnan University, Wuxi 214122, China

^b Jiangsu Key Laboratory of Anaerobic Biotechnology, Wuxi 214122, China

^c Jiangsu Collaborative Innovation Center of Water Treatment Technology and Material, Suzhou 215011, China

G R A P H I C A L A B S T R A C T



ARTICLE INFO

Keywords: Waste activated sludge Anaerobic digestion CO₂ sequestration Mineral carbonation Wollastonite

ABSTRACT

This study investigated the feasibility and performance of simultaneous in-situ CO₂ sequestration and CH₄ production promotion by wollastonite addition in sludge AD. A maximum CH₄ yield increment of 30.8% and maximum methane production rate increment of 64.9% with wollastonite addition at dosage of 16.25 g/L were achieved. CO₂ was efficient sequestered by wollastonite addition and resulted in a higher CH₄ content of 81.7%–82.4%. The mechanism of CO₂ sequestration by wollastonite was confirmed as Ca²⁺ release and subsequently carbonation based on cation and precipitates analysis. The results demonstrated that wollastonite could be applied as an effective additive for simultaneous in-situ CO₂ sequestration and CH₄ production promotion of sludge AD.

1. Introduction

As a byproduct of biological wastewater treatment, vast amounts of waste activated sludge (WAS) is produced during the operation of wastewater treatment plants (WWTPs) (Wang et al., 2015). In the U.S., the amount of annually generated sewage sludge is greater than 8 million (Liu et al., 2016). In China, the WAS yield increased year by

year with rapid urbanization and high-speed development of wastewater treatment industry, and has reached 55 million tons with water content of 80% in 2014 (Liu et al., 2017). WAS disposal is a critical and challenging issue accompanying wastewater treatment, but also provides an opportunity for energy and resource recovery owing to high organic content of the WAS. Harnessing energy from WAS could play a crucial role to reduce energy consumption of wastewater and WAS

https://doi.org/10.1016/j.biortech.2018.10.004 Received 15 August 2018; Received in revised form 29 September 2018; Accepted 1 October 2018 Available online 04 October 2018 0960-8524/ © 2018 Elsevier Ltd. All rights reserved.

^{*} Corresponding author at: School of Environment and Civil Engineering, Jiangnan University, Wuxi 214122, China. *E-mail address:* liuhe@jiangnan.edu.cn (H. Liu).

treatment (Coats and Wilson, 2017; Cornejo et al., 2016).

Anaerobic digestion (AD), comprises of hydrolysis, acidogenesis, acetogenesis, and methanogenesis processes, could effectively achieve mass reduction, pathogen reduction, and convert biodegradable organics to a combustible biogas composed principally of methane (CH₄) and carbon dioxide (CO_2). For its sludge stabilization, especially energy recovery ability, AD is the most widely used sludge treatment technology in developed countries. The energy produced by AD was estimated to cover 70-80% of energy consumption of a WWTP, if the AD process performs high efficiency (Jenicek et al., 2012). However, high content of CO₂ (15-60 vol%) may contained in the biogas produced by AD, with CH₄ content of 40-75% and trace amounts of other compounds like hydrogen sulfide and siloxanes (Garcia-Gutierrez et al., 2016). Utilization of biogas requires cleanup and upgrading processes, primarily, for CO2 removal (Lombardi and Carnevale, 2013; Makaruk et al., 2010). Current biogas upgrading technologies may cause a methane loss of 0.1-8% (Linville et al., 2016a), and increases biogas production costs by 20-72% (Linville et al., 2016b). In addition, CO₂ is usually released into the atmosphere during regeneration of the adsorbent media in the upgrading process, which aggravates climate warming. Therefore, its essential to develop in-situ CO₂ sequestration and biogas production enhancement technologies for AD process (Fernandez et al., 2017).

Carbonation of CO_2 is a process where CO_2 is fixed in the form of carbonates by divalent cations like Ca^{2+} , Mg^{2+} . In nature, alkaline silicate minerals such as wollastonite ($CaSiO_3$) and olivine (mainly Mg_2SiO_4) can potentially sequester CO_2 via mineral CO_2 carbonation. As carbonate precipitates forms under neutral and alkaline pH, and the release of divalent cations favors acidic pH, the rate of mineral CO_2 carbonation under ambient environmental conditions is usually very slow (Salek et al., 2013). Therefore, exposing alkaline silicate minerals to acid conditions to accelerate cations release, followed by carbonation in an alkaline environment can enhance mineral CO_2 sequestration. AD is essentially a two-stage system consisting of VFAs fermentation from complex organic compounds, and subsequent methanogenesis from the VFAs. Proton generated during VFAs fermentation can accelerated cations release from silicate minerals like wollastonite according to Eq. (1):

$$CaSiO_3 + 2H^+ \rightarrow Ca^{2+} + SiO_2 + H_2O$$
(1)

While methanogenesis can generate adequate alkalinity for carbonate precipitates formation (Salek et al., 2013). Therefore, developing in-situ CO₂ sequestration based on mineral carbonation in sludge AD systems should be a theoretically feasible way, which can conduct biogas upgrading during its production, and enhance the economic and environmental benefits of WAS AD.

Olivine has been demonstrated as an additive during sludge AD, and improve CH_4 content from 71.2%–75.9% to 74.9%–76.4% with in-situ CO₂ sequestration (Linville et al., 2016b). Trace element like Ni/Co did not impact on CO₂ sequestration by olivine (Linville et al., 2016a). The CH₄ production of sludge AD was also improved with olivine addition, probably owing to its pH buffering (Linville et al., 2016b). Wollastonite is another kind of silicate rock has broader distribution and cheaper price compared to olivine, which makes wollastonite more potential than olivine in practical engineering application of mineral CO₂ sequestration. In addition, cations release from silicate minerals is the key step limiting the performance of mineral CO₂ sequestration. The faster release of cations from wollastonite than from olivine was confirmed by its higher pH buffering ability during acidification (Lindeboom et al., 2013), indicated the higher CO_2 sequestration potential of wollastonite than olivine. Meanwhile, CaCO_3 (k_{sp} = 3.36 \times 10 $^{-9}$ at 25 °C) has lower solubility and higher stability than MgCO₃ ($k_{sp} = 6.82 \times 10^{-6}$ at 25 °C). Therefore, wollastonite may perform, theoretically, better than olivine on CO₂ sequestration in sludge AD, as well as on CH₄ production improvement owing to its higher pH buffering ability.

The main objective of this study is to investigate the feasibility and

performance of simultaneous in-situ CO₂ sequestration and CH₄ production promotion by wollastonite addition in sludge AD. Dynamic processes of intermediate VFAs production and conversion, methane production and content, Ca²⁺ release and consumption during sludge AD with wollastonite addition were revealed. Strategy for further application of CO₂ sequestration with wollastonite supplementation in sludge AD was also discussed.

2. Materials and methods

2.1. Sludge substrate, inoculum, and wollastonite

The WAS for digestion was the excess sludge of a local wastewater treatment plant (WWTP). The sludge was taken immediately after dewatering by a belt press filter in the WWTP, and stored under 4 °C until use. The inoculum was anaerobic granular sludge taken from an upflow anaerobic sludge bed (UASB) reactor, with sludge retention time of 120 days, in 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) concentration of 73 g/L, and was diluted to TS concentration of 60 g/L before use. Thermal pretreatment, 100 °C for 12 h, was adopted for half of the sludge after dilution. The seed anaerobic sludge, i.e. inoculum, had pH of 7.2, TS concentration of 61 g/L, VS concentration of 36 g/L. Wollastonite in 120 mesh was purchased from a mining company in China and used for CO₂ sequestration. The average particle size of the wollastonite was 21.0 µm. The main element composition of the wollastonite detected by energy dispersive spectrometer (EDS) was Ca 29.92% (wt%), O 43.82%, C 9.06%, P 0.01%, Si 16.29%, Mg 0.28%, Fe 0.21%, and Al 0.30%. The X-ray diffraction (XRD) pattern of the wollastonite fit well with standard peaks in the database (PDF#27-1064).

2.2. Anaerobic digestion operation

The AD experiments were conducted in 1.6 L glass digesters with working volume of 1.2 L under temperature of 35 °C. Two types of sludge substrate, i.e. the un-pretreated WAS and thermal pretreated WAS, were used. 1 L of the un-pretreated WAS and thermal pretreated WAS were fed into different digesters, and named as S and THS, respectively. Subsequently, 200 mL seed anaerobic sludge was inoculated into each digester. The pH of the mixture was adjusted to neutral with HCl. A parallel group of digesters fed with above substrates were added with 19.5 g wollastonite per digester, and named as S + W, and THS + W, respectively. The digesters were degassed with nitrogen gas for 20 min to eliminate dissolved oxygen in the mixture and the oxygen gas in the headspaces before digestion. The mixture in each digester were stirred with an agitator under speed of 120 rpm continuously. A gas bag was installed on the top of each digester for biogas collection. The AD experiments were conducted under batch mode and terminated according to the tenuous increase of biogas production after 12 days operation. The gas and liquid samples were collected from each digester periodically for analysis.

2.3. Analysis methods

195

Total solids (TS) and volatile solids (VS) were measured with gravimetric method. For liquid sample analysis, the samples were pretreated by filtrating with $0.45 \,\mu\text{m}$ filter. After filtration, soluble chemical oxygen demand (SCOD), pH, total alkalinity (TA), NH₄⁺-N, and PO₄³⁺ were analyzed according to the standard methods issued by the State Environmental Protection Administration of China (2002). Free ammonia nitrogen (FAN) was calculated according to Angelidaki and Ahring (1993).

Volatile fatty acids (VFAs) in the filtrated liquid samples were measured by gas chromatograph method according to Ma et al. (2017). A GC-2010 (Shimadzu, Japan) equipped with a flame ionization detector and an auto injector (AOC-20i, Shimadzu, Japan) was used. The column adopted in the detection was a fused silica capillary (PEG-20M, $30 \text{ m} \times 0.32 \text{ mm} \times 0.50 \text{ }\mu\text{m}$). The samples were acidized by 3 M phosphoric acid and added with 4-methyl-valeric acid as an internal standard before injection. The temperature program of the GC column was 80 °C for 3 min, then increased by 15 °C/min, and held for 3 min at final temperature of 210 °C. The temperature of both injection port and detector was set at 250 °C. The total VFAs (TVFA) concentration was calculated by summing up all of detected individual VFA. The Ca²⁺ concentration was measured by an inductively coupled plasma emission spectrometer (ICP, Optima 8300, PerkinElmer, USA). The volume of produced biogas was measured by displacement of saturated aqueous NaCl in a graduated measuring cylinder (Abouelenien et al., 2009). The methane (CH_4) and carbon dioxide (CO_2) content was measured by a gas chromatograph (GC9790II, Fuli, China). The percent of CH₄ and CO2 was normalized to assume 100% biogas (methane and carbon dioxide only) was produced. The microscopic photos were taken by a scanning electron microscope (SEM, SU1510, Hitachi, Japan). Particle size was measured by a laser particle size distribution instrument (BT-2003, Bettersize, China). The element composition was analyzed by an EDS (SU1510, Hitachi, Japan). The XRD analysis was conducted on a D2 PHASER (Bruker AXS, Germany). Capillary suction time (CST) value was measured by a capillary suction timer (Type 304M, Triton Electronics, UK).

2.4. Modelling of methane production

The methane production curves were fitted to modified Gompertz equation in order to obtain the kinetic parameters. The modified Gompertz equation (Nopharatana et al., 2007) was shown in Eq. (2).

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

In the model, *B* is the cumulative methane production (ml), *P* is the maximum methane production potential (ml), R_m is the maximum methane production rate (ml/h), λ is the duration of lag phase (h), and *t* is the duration of the digestion at which cumulative methane production, *B*, is calculated (h). The fitting was conducted by software Origin 8.0, and adjusted R² (adj. R²) was calculated to evaluate the accuracy of the model.

3. Results & discussion

3.1. Methane production enhancement and carbon dioxide reduction

The cumulative CH_4 production and CO_2 production during sludge AD are shown in Fig. 1. The amount of produced methane from the thermal pretreated sludge was significantly more than that from the unpretreated sludge, which confirmed the methane production

Table 1

Model fitting results of methane production data using the modified Gomepertz Equation.

	P (ml)	Rm (ml/h)	λ (h)	adj. \mathbb{R}^2
S S + W THS THS + W	$\begin{array}{rrrrr} 1125.37 \ \pm \ 33.91 \\ 1195.16 \ \pm \ 31.59 \\ 2052.81 \ \pm \ 223.03 \\ 2601.79 \ \pm \ 110.74 \end{array}$	$\begin{array}{r} 8.52\ \pm\ 0.74\\ 9.39\ \pm\ 0.74\\ 9.83\ \pm\ 1.55\\ 16.21\ \pm\ 1.59\end{array}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	0.9874 0.9898 0.9376 0.9799

improvement owing to enhanced hydrolysis by sludge pretreatment (Ariunbaatar et al., 2014; Neumann et al., 2016). The methane production of wollastonite added sludge AD systems were 2575.8 mL for THS + W and 1234.3 mL for S + W, higher than that of control sludge AD systems (1969.3 mL for THS and 1164.7 mL for S). Wollastonite supplementation increased methane production by 30.8% for the AD of thermal pretreated sludge and 5.9% for the AD of un-pretreated sludge. The effect of wollastonite supplementation on CH₄ production rate was also evaluated based on modelling. By fitting CH₄ production data to modified Gomepertz model, the estimated lag phase (λ) and maximum CH₄ production rate (R_m) were obtained (shown in Table 1). The λ was not shorten by wollastonite supplementation, as it was already very short in the controls. However, with wollastonite addition, the R_m was increased by 10.2% and 64.9% for un-pretreated sludge and thermal pretreated sludge AD, respectively. It indicated that both CH₄ yield and CH₄ production rate could be improved by wollastonite supplementation.

As shown in Fig. 1b, the cumulative CO_2 production of S + W was lower than that of S. The cumulative CO_2 production of THS + W was higher than that of THS by 19.4%. The increased CO₂ production (19.4%) was lower than the increased CH₄ production (30.8%), with wollastonite addition in the AD of thermal pretreated sludge. It indicated that when equal amount of methane produced in THS + W and THS, less CO₂ was generated in THS + W compared to THS. Correspondingly, the CO_2 content in produced biogas of THS + W (18.3%) was lower than that of THS (19.7%), consistent with the lower CO₂ content of S + W (17.6%) than that of S (23.7%, as shown in Table 2). According to the decreased CO2 content, it could be deduced that mineral CO₂ sequestration based on wollastonite addition was achieved in both S + W and THS + W. The mineral CO_2 carbonation was confirmed by precipitates analysis (data shown later). More CO₂ produced in THS + W was owing to the improvement of biogas production by wollastonite addition, though mineral CO₂ carbonation was also achieved. If assuming the gas content before CO₂ carbonation in wollastonite added AD systems were consistent to the corresponding controls without woll astonite addition, the sequestered CO_2 in $\mathrm{S}+\mathrm{W}$ and THS + W were estimated as 119.8 mL and 54.8 mL, and account for 31.2% and 8.7% of the generated CO₂, respectively.



Fig. 1. (a) Cumulative CH_4 and (b) cumulative CO_2 production of sludge AD.

Table 2

CH₄ and CO₂ content in produced biogas.

	CH4 (%)	CO ₂ (%)
S	76.3	23.7
S + W	82.4	17.6
THS	80.3	19.7
THS + W	81.7	18.3

The dosage of wollastonite in this study was 19.5 g per digester, i.e. 16.25 g/L, which was lower than the dosage (25–50 g/L) of fine olivine (< 120 mesh) used in the reported study (Linville et al., 2016b). However, the 30.8% of methane improvement in this study was much higher than that improved by olivine addition (< 7%) in mesophilic AD. Wollastonite performed better CH₄ production improvement than olivine. Compared to other additives reported promoting CH₄ production, wollastonite also showed better competitiveness. Five types of zeolites were tested for its impact on sludge AD, only natural mordenite increased methane production under dosage of 50 g/L (Tada et al., 2005). WAS incineration bottom ash addition could increase biogas production by up to 3.5 times under dosage of 12–120 g/g VS (Lo et al., 2012). The adopted dosage was too high to be scaled up for actual engineering application. In relative low dosage range, a methane production increment of 26.6% was achieved (Yin et al., 2018), which was still slightly lower than that improved by wollastonite in this study. Moreover, the bottom ash dosage of 0.9 g/g TS (Yin et al., 2018) also was nearly 3 times higher than wollastonite dosage of 0.325 g/g TS in this study. The reduced CO_2 content, 6.1% and 1.4% for the two types of sludge, with wollastonite addition in the AD systems in this study were also higher than that achieved by olivine supplementation (1.2%-3.7%) under a higher dosage (Linville et al., 2016b). Better performance of CO₂ sequestration and CH₄ production promotion by wollastonite than olivine in sludge anaerobic digestion was revealed.

3.2. Effect of wollastonite on VFAs production and conversion

The profiles of SCOD, TVFA and VFAs concentrations are shown in Fig. 2. The initial SCOD and TVFA of pretreated sludge AD group, THS and THS + W, were much higher than that of un-pretreated sludge AD group, S and S + W, owing to the excellent hydrolysis performance of thermal pretreatment (Ennouri et al., 2016). For un-pretreated sludge AD, the SCOD in S increased slightly during digestion, while the SCOD in S + W increased more than that in the S. As more CH₄ was produced in S + W than in S (Fig. 1a), which means more organic matters in the liquid phase were converted to CH_4 , the higher SCOD in S + W indicated more organic matters was hydrolyzed from sludge, and means that the hydrolysis of the sludge was enhanced with wollastonite supplementation. For thermal pretreated sludge AD, the SCOD in THS and THS + W decreased gradually during digestion. The thermal pretreatment released high concentration of organic matters in the liquid phase, and enhanced methane production, resulting the decrease of SCOD during digestion. The TVFA peaked at hour 15 in THS and THS + W with concentration of 2.25 g/L and 2.08 g/L, respectively. It indicated that a higher rate of acidification than the rate of methane production from VFAs in the first 15 h digestion, while the rate of methane production overcome that of acidification afterward. The TVFA in wollastonite supplemented AD, THS + W, was lower than that in AD without wollastonite addition, THS. The difference of TVFA concentration between THS and THS + W became bigger along with digestion progress, indicating a higher VFA conversion rate was achieved with wollastonite addition. It revealed that wollastonite addition could enhance hydrolysis and methanogenic activity in sludge AD, and resulting higher methane production (as shown in Fig. 1).

The components of the VFAs produced in the digesters included acetate, propionate, isobutyrate, *n*-butyrate, isovalerate, and *n*-valerate.

As low concentration of VFAs were accumulated in un-pretreated sludge AD systems, the effect of wollastonite on VFAs composition seems irregular. In thermal pretreated sludge AD, THS, acetate was the dominant acid with concentration of 0.79 g/L when the TVFA accumulated most at hour 15. After 60 h digestion, acetate was significant reduced to 0.26 g/L, while propionate increased to 0.58 g/L, became the dominant acid, and kept relative stable afterward. Wollastonite supplementation significant decreased propionate concentration in THS + W, and resulting lower TVFA compare to THS. The production and transformation of propionate and acetic acid were mainly based on different microorganisms and different metabolic pathways (Ma et al., 2017; Song et al., 2018). The degradation of propionic acid was enhanced by addition of sulfate as an external electron acceptor (Oiao et al., 2016). If the enhanced degradation of propionic acid with wollastonite addition caused by microbial community change or electron transfer improvement need further investigation.

3.3. Change of digestion environment with wollastonite addition

The pH profiles of the digesters are shown in Fig. 3a. The initial pH of the digesters was similar, ranged in 6.82-6.88. In un-pretreated sludge AD, S, the pH increased gradually throughout the digestion. In thermal pretreated sludge AD, THS, the pH was decreased to 6.67 with first 15 h, then increased substantially to 7.08 at hour 36 and kept gradual increase afterward. The decreased pH at hour 15 was consistent with the increased TVFA, and could attribute to dissociation of VFAs. Wollastonite increased the pH of the digesters immediately after its addition, and kept higher in S+W and THS+W compared to the corresponding control. The pH buffering ability of wollastonite was revealed by THS + W, in which the pH was not decreased with VFAs accumulation at hour 15. Both acidic and alkaline condition could inhibit methanogenic activity during sludge digestion (Montanes et al., 2014; Yang et al., 2015; Zhang et al., 2018), though alkaline condition was considered to benefit VFAs production (Liu et al., 2012). The buffering of wollastonite avoided acidic condition of the digester, the increased pH in THS + W was lower than 7.5 at the end of digestion, which well facilitate methane production. The TA concentration in S + W and THS + W was improved with the increased pH and enhanced methanogenic activity (Fig. 3b). The highest TA concentration in THS + W was 3822.8 mg/L as CaCO₃, which was much lower than the inhibition concentration (10,000 mg/L as CaCO₃) for methanogenesis (Lin et al., 2013). The addition of wollastonite did not significantly influence the concentration of NH4+-N (Fig. 4a). The FAN was increased in S + W and THS + W owing to the improved pH with wollastonite addition (Fig. 4b). However, the highest FAN in THS + W was 23.9 mg/L, still much lower than the considered threshold for methanogenesis inhibition (Chen et al., 2008; Duan et al., 2012).

As Ca²⁺ release from wollastonite could remarkably influence CO₂ sequestration in sludge AD, the variation of Ca^{2+} concentration in the digesters was investigated (shown in Fig. 5a). Substantial release of Ca^{2+} was achieved in each digesters in the first 15 h, as the Ca^{2+} concentration significant increased and reached 153.6 mg/L, 122.8 mg/ L, 111.5 mg/L, and 108.3 mg/L in THS + W, THS, S + W, and S, respectively. The increased Ca²⁺ concentration in the digesters without wollastonite addition indicated the existence of calcium in the sludge. The highest Ca^{2+} concentration detected in THS + W and S + W was 31.2 mg/L and 19.2 mg/L higher than that in THS and S, respectively. The released Ca²⁺ with wollastonite addition might be much higher than the detected value, as CO₂ carbonation could happen during Ca²⁺ release under pH approximate neutral (Ebrahimi et al., 2018). The source of released Ca^{2+} influences that if it could achieve CO_2 sequestration. WAS usually contains some CaCO₃, which accumulated during wastewater treatment. If the released Ca^{2+} in S and THS was from CaCO₃ in sludge, CO₂ sequestration would not achieve as CO₂ also released when Ca²⁺ release. Therefore, the cations from external silicate mineral, i.e. Ca²⁺ from wollastonite in this study, was crucial for



Fig. 2. Profiles of (a) SCOD, (b) TVFA during sludge AD, and the variation of VFAs concentration in (c) S, (d) S + W, (e) THS, and (f) THS + W.

CO₂ sequestration.

It was reported that 2.5 g/L CaCl₂ (900.9 mg/L Ca²⁺) increased the biogas production from anaerobic digestion of municipal solid waste by 31.3% (Kumar et al., 2016), and 500 mg/L Ca²⁺ significantly enhanced the methane production from anaerobic digestion of municipal solid waste leachate (Dang et al., 2014). However, higher concentration of 5.0 g/L CaCl₂ (1801.8 mg/L Ca²⁺) and 2000 mg/L Ca²⁺ decreased the biogas production from anaerobic digestion of municipal solid waste and municipal solid waste leachate, respectively (Dang et al., 2014; Kumar et al., 2016). A moderate Ca²⁺ concentration improvement is proved to enhance anaerobic digestion, while high concentration of Ca²⁺ deteriorates AD performance owing to suppression of acetoclastic methanogenesis (Dang et al., 2014; Yin et al., 2018). The improved Ca²⁺ concentration (111.5–154.0 mg/L) was far below the suppression concentration, and could be another factor for methane production

enhancement of anaerobic digestion by wollastonite addition besides pH buffering.

The variation of $PO_4^{3^-}$ in the digesters are shown in Fig. 5b. The concentration of $PO_4^{3^-}$ in the digesters fed with thermal pretreated sludge were much higher than that in the digesters fed with un-pretreated sludge. Comparing the two digesters fed with un-pretreated sludge, the $PO_4^{3^-}$ concentration was slightly higher in S + W than in S. The improved $PO_4^{3^-}$ concentration in S + W could be attributed to the enhanced hydrolysis by wollastonite addition, as more organic matters was hydrolyzed and dissolved (Fig. 2) and could increase $PO_4^{3^-}$ concentration in THS + W was lower than that in THS. The decreased $PO_4^{3^-}$ concentration in THS + W was owing to the formation of Ca-phosphate precipitates with the reaction between Ca²⁺ and $PO_4^{3^-}$, as Ca-phosphate is very easy to generate in liquid environment (Lee et al., 2013; Tervahauta et al.,



Fig. 3. Profiles of (a) pH and (b) total alkalinity during sludge AD.

2014). It should be emphasized that Ca-phosphate should also generated in S + W, though PO_4^{3-} concentration in S + W was higher than that in S.

3.4. Carbon dioxide sequestration with calcium carbonate formation

Precipitates formed in wollastonite supplemented digesters, both S + W and THS + W. During digestion, the initial formed fine precipitates firstly attached to the surface of the sludge. With growth of the crystals, precipitate shells formed on sludge particles. Finally, the shells detached from sludge particles after "maturity" of the shells under stirring. The diameter of used anaerobic granular sludge mainly ranged in 2-4 mm. The size of shell particles was approximate 3 times of the granular sludge, with the thickness of the shell approximate 2-3 mm. Owing to the hydraulic shear under stirring, the convex sides of the formed precipitate shells were relatively smooth. While the concave sides of the shells were much rougher. The element composition of the formed precipitates and residual wollastonite were measured by EDS (Table 3). Ca, O, C, and P were the four main elements in the precipitates, which was well consistent with the element composition of predicted products, i.e. CaCO3 and Ca3(PO4)2. The Ca content in the residual wollasonite was 2.36%, which was substantially lower than that in the initial wollastonite (29.92%), indicated the well release of Ca from the surface of added wollastonite. The higher content of O and Si in the residual wollastonite compared to the initial one was also in line with the formation of SiO₂ along with Ca release. The XRD pattern of formed precipitate was generally consistent with the combined standard patterns of calcium phosphate (PDF#17-0498) and vaterite (PDF#33-0268), a kind of CaCO₃ crystal. The XRD pattern of the residual wollastonite was well fit with the combined standard patterns of

wollastonite (PDF#27-1064) and silicon oxide (PDF#76-0931). The element composition and XRD pattern analysis well revealed the process of Ca²⁺ release from the wollastonte and CaCO₃ formation during sludge AD, which confirmed the achievement of mineral CO2 carbonation in the ADs with wollastonite addition. The precipitation of Ca²⁺ with PO₄³⁻ happened along with CaCO₃, similar with the co-precipitation of Ca^{2+} with CO_3^{2-} during phosphorus recovery by calcium phosphate granulation (Tervahauta et al., 2014). For improvement of CO₂ sequestration, the inhibition of calcium phosphate precipitation should be investigated in further. In addition, precipitation of calcium salt could be prevented with chelating agents. The remained Ca²⁺ in the liquid after digestion (77.3-127.8 mg/L, Fig. 5a), might be owing to the chelation by certain compounds like humic acid in the digesters. A higher released Ca²⁺ amount may further enhance the performance of CO₂ sequestration by carbonation. Considering the pH variation during sludge AD, a higher Ca²⁺ release rate during VFAs fermentation at initial stage of AD might increase the released Ca²⁺ amount. As reactive surface area and temperature are two main factors besides hydronium ion activity affect the release rate of Ca^{2+} from wollastonite (Arinicheva et al., 2018), increasing total reactive surface area with increased wollastonite dosage and operating sludge AD under a higher temperature could be potential ways to further enhance CO₂ sequestration. Using finer wollastonite can also increase reactive surface area, however, the separation of residual wollastonite from AD might be difficult.

The CST of the digested sludge in S, S + W, THS, and THS + W were 406.4 s, 424.1 s, 1046.1 s, and 1071.8 s, respectively, indicated that the dewaterability of the sludge was very slightly affected by wollastonite addition. Prior to sludge dewatering and subsequent disposal, the residual wollastonite and the formed precipitates could be substantially



Fig. 4. Profiles of (a) NH₄⁺-N and (b) FAN concentration during sludge AD.



Fig. 5. Profiles of (a) Ca^{2+} and (b) PO_4^{3-} concentration during sludge AD.

 Table 3

 The element composition of formed precipitates and residual wollastonite in sludge AD experiment.

Elements (wt%)	Precipitates in S + W	Precipitates in THS + W	Residual wollastonite in THS + W	Initial wollastonite
Ca	24.77	20.63	2.36	29.92
0	34.47	44.79	49.09	43.82
С	15.42	16.62	10.94	9.06
Р	12.09	5.48	0.39	0.01
Si	2.44	6.33	32	16.29
Mg	1.17	0.36	0.43	0.28
Fe	7.11	4.33	1.94	0.21
Al	2.53	1.46	2.85	0.3

removed by sedimentation based on the different density of sludge and minerals. The sludge dewatering and disposal processes will not be substantially impacted by wollastonite addition. The separated wollastonite and precipitates might be reused as building materials after suitable processing, which could greatly compensate the cost of wollastonite purchase.

4. Conclusions

 CO_2 sequestration and CH_4 production enhancement by wollastonite in sludge AD was demonstrated in this study. Supplementation of wollastonite at a low dosage of 16.25 g/L promoted sludge hydrolysis and methanogenesis with R_m increment of 10.2%–64.9%, and achieved a maximum increment of cumulative CH_4 production by 30.8%. CO_2 was sequestered by precipitation of $CaCO_3$ and resulted in a highest CH_4 content of 82.4%. Coupling mineral CO_2 sequestration in sludge AD achieved a better energy recovery and contributed to mitigation of greenhouse effect, showing good economic and environmental benefits.

Acknowledgements

This study was supported by National Natural Science Foundation of China (No. 51678280, No. 51708253), and Special Program for the Taihu Lake Protection of Jiangsu Province (JSZC-G2016-345).

Conflicts of interest

None.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biortech.2018.10.004.

References

- Abouelenien, F., Kitamura, Y., Nishio, N., Nakashimada, Y., 2009. Dry anaerobic ammonia-methane production from chicken manure. Appl. Microbiol. Biot. 82, 757–764.
- Angelidaki, I., Ahring, B.K., 1993. Thermophilic anaerobic-digestion of livestock waste the effect of ammonia. Appl. Microbiol. Biot. 38, 560–564.
- Arinicheva, Y., Gausse, C., Neumeier, S., Brandt, F., Rozov, K., Szenknect, S., Dacheux, N., Bosbach, D., Deissmann, G., 2018. Influence of temperature on the dissolution kinetics of synthetic LaPO₄-monazite in acidic media between 50 and 130 degrees C. J. Nucl. Mater. 509, 488–495.
- Ariunbaatar, J., Panico, A., Esposito, G., Pirozzi, F., Lens, P.N.L., 2014. Pretreatment methods to enhance anaerobic digestion of organic solid waste. Appl. Energy 123, 143–156.
- Chen, Y., Cheng, J.J., Creamer, K.S., 2008. Inhibition of anaerobic digestion process: a review. Bioresour. Technol. 99, 4044–4064.
- Coats, E.R., Wilson, P.I., 2017. Toward nucleating the concept of the water resource recovery facility (WRRF): perspective from the principal actors. Environ. Sci. Technol. 51, 4158–4164.
- Cornejo, P.K., Zhang, Q., Mihelcic, J.R., 2016. How does scale of implementation impact the environmental sustainability of wastewater treatment integrated with resource recovery? Environ. Sci. Technol. 50, 6680–6689.
- Dang, Y., Zhang, R., Wu, S., Liu, Z., Qiu, B., Fang, Y., Sun, D., 2014. Calcium effect on anaerobic biological treatment of fresh leachate with extreme high calcium concentration. Int. Biodeterior. Biodegrad. 95, 76–83.
- Duan, N., Dong, B., Wu, B., Dai, X., 2012. High-solid anaerobic digestion of sewage sludge under mesophilic conditions: feasibility study. Bioresour. Technol. 104, 150–156.
- Ebrahimi, A., Saffari, M., Hong, Y., Milani, D., Montoya, A., Valix, M., Minett, A., Abbas, A., 2018. Mineral sequestration of CO₂ using saprolite mine tailings in the presence of alkaline industrial wastes. J. Clean. Prod. 188, 686–697.
- Ennouri, H., Miladi, B., Zahedi Diaz, S., Fernandez Guelfo, L.A., Solera, R., Hamdi, M., Bouallagui, H., 2016. Effect of thermal pretreatment on the biogas production and microbial communities balance during anaerobic digestion of urban and industrial waste activated sludge. Bioresour. Technol. 214, 184–191.
- Fernandez, Y.B., Soares, A., Koch, K., Vale, P., Cartmell, E., 2017. Bioconversion of carbon dioxide in anaerobic digesters for on-site carbon capture and biogas enhancement – a review. Crit. Rev. Environ. Sci. Technol. 47, 1555–1580.
- Garcia-Gutierrez, P., Jacquemin, J., McCrellis, C., Dimitriou, I., Taylor, S.F.R., Hardacre, C., Allen, R.W.K., 2016. Techno-economic feasibility of selective CO₂ capture processes from biogas streams using ionic liquids as physical absorbents. Energy Fuels 30, 5052–5064.
- Jenicek, P., Bartacek, J., Kutil, J., Zabranska, J., Dohanyos, M., 2012. Potentials and limits of anaerobic digestion of sewage sludge: energy self-sufficient municipal wastewater treatment plant? Water Sci Technol. 66, 1277–1281.
- Kumar, S., Das, A., Srinivas, G.L.K., Dhar, H., Ojha, V.K., Wong, J., 2016. Effect of calcium chloride on abating inhibition due to volatile fatty acids during the start-up period in anaerobic digestion of municipal solid waste. Environ. Technol. 37, 1501–1509.
- Lee, S.-H., Yoo, B.-H., Kim, S.-K., Lim, S.J., Kim, J.Y., Kim, T.-H., 2013. Enhancement of struvite purity by re-dissolution of calcium ions in synthetic wastewaters. J. Hazard. Mater. 261, 29–37.
- Lin, Y., Lu, F., Shao, L., He, P., 2013. Influence of bicarbonate buffer on the methanogenetic pathway during thermophilic anaerobic digestion. Bioresour. Technol. 137, 245–253.
- Lindeboom, R.E.F., Ferrer, I., Weijma, J., van Lier, J.B., 2013. Silicate minerals for CO₂ scavenging from biogas in autogenerative high pressure digestion. Water Res. 47, 3742–3751.
- Linville, J.L., Shen, Y., Urgun-Demirtas, M., Snyder, S.W., 2016b. Effect of particle size and doses of olivine addition on carbon dioxide sequestration during anaerobic digestion of sewage sludge at ambient and mesophilic temperatures. Process Biochem. 51, 59–72.
- Linville, J.L., Shen, Y., Schoene, R.P., Nguyen, M., Urgun-Demirtas, M., Snyder, S.W., 2016a. Impact of trace element additives on anaerobic digestion of sewage sludge

with in-situ carbon dioxide sequestration. Process Biochem. 51, 1283-1289.

Liu, H., Wang, J., Liu, X., Fu, B., Chen, J., Yu, H.-Q., 2012. Acidogenic fermentation of proteinaceous sewage sludge: effect of pH. Water Res. 46, 799–807.

- Liu, H., Wang, Y., Wang, L., Yu, T., Fu, B., Liu, H., 2017. Stepwise hydrolysis to improve carbon releasing efficiency from sludge. Water Res. 119, 225–233.
- Liu, J., Yu, D., Zhang, J., Yang, M., Wang, Y., Wei, Y., Tong, J., 2016. Rheological properties of sewage sludge during enhanced anaerobic digestion with microwave-H₂O₂ pretreatment. Water Res. 98, 98–108.
- Lo, H.M., Chiu, H.Y., Lo, S.W., Lo, F.C., 2012. Effects of micro-nano and non micro-nano MSWI ashes addition on MSW anaerobic digestion. Bioresour. Technol. 114, 90–94.
- Lombardi, L., Carnevale, E., 2013. Economic evaluations of an innovative biogas upgrading method with CO₂ storage. Energy 62, 88–94.
- Ma, H., Liu, H., Zhang, L., Yang, M., Fu, B., Liu, H., 2017. Novel insight into the relationship between organic substrate composition and volatile fatty acids distribution in acidogenic co-fermentation. Biotechnol. Biofuels 10, 137.
- Makaruk, A., Miltner, M., Harasek, M., 2010. Membrane biogas upgrading processes for the production of natural gas substitute. Sep. Purif. Technol. 74, 83–92.
- Montanes, R., Perez, M., Solera, R., 2014. Anaerobic mesophilic co-digestion of sewage sludge and sugar beet pulp lixiviation in batch reactors: effect of pH control. Chem. Eng. J. 255, 492–499.
- Neumann, P., Pesante, S., Venegas, M., Vidal, G., 2016. Developments in pre-treatment methods to improve anaerobic digestion of sewage sludge. Rev. Environ. Sci. Biol. 15, 173–211.
- 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 Manage. 27, 595–603.
- Qiao, W., Takayanagi, K., Li, Q., Shofie, M., Gao, F., Dong, R.J., Li, Y.Y., 2016. Thermodynamically enhancing propionic acid degradation by using sulfate as an external electron acceptor in a thermophilic anaerobic membrane reactor. Water Res.

106, 320-329.

- Salek, S.S., Kleerebezem, R., Jonkers, H.M., Witkamp, G.-J., van Loosdrecht, M.C.M., 2013. Mineral CO₂ sequestration by environmental biotechnological processes. Trends Biotechnol. 31, 139–146.
- Song, C.H., Li, M.X., Qi, H., Zhang, Y.L., Liu, D.M., Xia, X.F., Pan, H.W., Xi, B.D., 2018. Impact of anti-acidification microbial consortium on carbohydrate metabolism of key microbes during food waste composting. Bioresour. Technol. 259, 1–9.
- State Environmental Protection Administration of China, 2002. Standard Methods for the Analysis of Water and Wastewater. China Environmental Science Publishing House, Beijing.
- Tada, C., Yang, Y., Hanaoka, T., Sonoda, A., Ooi, K., Sawayama, S., 2005. Effect of natural zeolite on methane production for anaerobic digestion of ammonium rich organic sludge. Bioresour. Technol. 96, 459–464.
- Tervahauta, T., van der Weijden, R.D., Flemming, R.L., Leal, L.H., Zeeman, G., Buisman, C.J.N., 2014. Calcium phosphate granulation in anaerobic treatment of black water: a new approach to phosphorus recovery. Water Res. 48, 632–642.
- Wang, Y., Gui, C., Ni, X., Chen, M., Wei, Y., 2015. Multivariate analysis of sludge disintegration by microwave-hydrogen peroxide pretreatment process. J. Hazard. Mater. 283, 856–864.
- Yang, L., Huang, Y., Zhao, M., Huang, Z., Miao, H., Xu, Z., Ruan, W., 2015. Enhancing biogas generation performance from food wastes by high-solids thermophilic anaerobic digestion: Effect of pH adjustment. Int. Biodeterior. Biodegrad. 105, 153–159.
- Yin, C., Shen, Y., Zhu, N., Huang, Q., Lou, Z., Yuan, H., 2018. Anaerobic digestion of waste activated sludge with incineration bottom ash: enhanced methane production and CO₂ sequestration. Appl. Energy 215, 503–511.
- Zhang, W., Dai, K., Xia, X.-Y., Wang, H.-J., Chen, Y., Lu, Y.-Z., Zhan, F., Zeng, R.J., 2018. Free acetic acid as the key factor for the inhibition of hydrogenotrophic methanogenesis in mesophilic mixed culture fermentation. Bioresour. Technol. 264, 17–23.