An Integrated Approach to Biogas Production and Phosphorus Recovery from Waste Activated Sludge: Effect of Temperature

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Abstract
An integrated approach to biogas production through anaerobic digestion and phosphorus recovery with the struvite precipitation method was reported in this paper. The effect of digestion temperature in the range of 20 to 55^{o}C on the recovery efficiency of biogas and phosphorus was investigated. The results showed that the digestion temperature played an important role in the production of biogas. The production rate of biogas significantly increased with the increasing of temperature form 20 to 45^{o}C, but decreased subsequently with a further increase of temperature. Although the final yield of biogas was the poorest at the digestion temperature of 20^{o}C, but the maximum concentration of PO_4^{3-}-P was achieved at the same temperature. Subsequently, the phosphorus in the digested liquids harvested from the different digestion temperatures was recovered by the struvite crystallization method. The analysis of scanning electron microscope showed that compared with other digestion temperatures, 45^{o}C was favorable for the growth of high crystal struvite, and more regular and large crystals were formed in the precipitate product. The maximum values of the biomethane yield and the recovery ratio of soluble total P were both obtained at the digestion temperature of 45^{o}C; and they reached 398 mL/g-VS and 92.9%, respectively.

Keywords
Waste activated sludge; biogas; phosphorus; recovery; temperature

INTRODUCTION

In the past few decades, the activated sludge process has been applied to remove nutrients from wastewater worldwide (Liu and Tay, 2001; Amanatidou et al., 2015). However, a large amount of waste activated sludge (WAS) is produced from this process (Yan et al., 2013). Increasing attention has been given to recover useful substance from WAS since environmental regulations are being more and more stringent in relation to the treatment and disposal of WAS (Kavitha et al., 2016; Su et al., 2016).

WAS contains a high content of organic substance such as protein, carbohydrate and lipids, which can be used as a substrate to produce biogas through anaerobic digestion (Liu et al., 2009). Most of the reported studies on the production of biogas from WAS through anaerobic digestion mainly focus on environmental factors and operation parameters, such as pH, substrate concentration, C/N, and so on (Mao et al., 2015). Besides organic substance, some important nutrition such as phosphorus is rich in WAS (Tong and Chen, 2009). Recently, it is considered as an effective way to recover phosphorus in the form of struvite from waste or wastewater to reduce phosphorus discharge into ecological systems (Jensen et al., 2016; Jin et al., 2009). However, little information can be found on the biogas production combining with the phosphorus recovery from WAS (Chen et al., 2013; Cieslik et al., 2015).

Temperature is a major factor affecting anaerobic digestion (Alvarez and Lide, 2008). Temperature can affect microbial abundance, activity and interactions in anaerobic digestion, which in turns affect anaerobic biodegradability of WAS and the operation stability of anaerobic digestion (Lin et al., 2016). However, most of the researchers only reported the effect of temperature on the production of biogas (Deng et al., 2016; Chae et al., 2008). Few studies discussed the effect of temperature on the liberation of phosphorus from WAS during anaerobic digestion. Therefore, this paper addressed an integrated approach to biogas production through anaerobic digestion and phosphorus recovery with the struvite crystallisation method. The effect of temperature on the production of biogas and the release of phosphorus during anaerobic digestion was investigated. Subsequently, the morphologies of precipitate products harvested during struvite crystallisation were analyzed by scanning electron microscope (SEM). Also, the recovery efficiency of biogas and phosphorus was analyzed.

MATERIAL AND METHODS

Waste activated sludge and seed sludge

WAS was obtained from Qinghe Sewage Treatment Plant in Beijing, China. Seed sludge was collected from an Up-flow Anaerobic Sludge Bed at our laboratory. The characteristics of WAS and seed sludge were shown in Table 1.

Table 1. Characteristics of waste activated sludge and seed sludge.

Items	Waste activated sludge	Seed sludge
Total solids (wt %)	20.0	5.1
Volatile solids (wt % dry basis)	57.8	3.9
Total P (mg/g-dry basis)	21.4	21.5
PO_4^{3-}-P (mg/L)	28	31

Process design and experimental operation

The integrated process of biogas production and phosphorus recovery consisted of two main treatment steps. Firstly, anaerobic digestion was adopted to hydrolyze organic substance, mobilise orthophosphate and generate biogas from WAS; secondly, the struvite reaction crystallization process was used to recover phosphorus from the digested liquid. A process flow diagram of the experimental setup was shown in Figure 1.

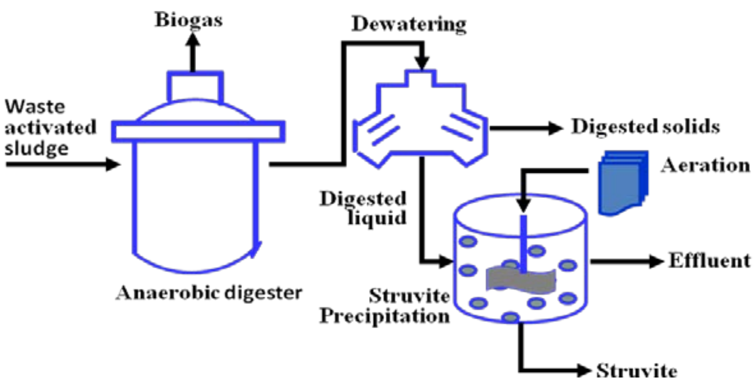

Figure 1. Integrated process flow diagram of the experimental setup for biogas production and recover phosphorus.

Anaerobic digestion. Anaerobic digestion of WAS was operated in batch tests. The total volume of anaerobic digester was 1000 mL, with an effective volume of 650 mL. Deionized water was added into each anaerobic digester to adjust the content of total solids in the fermentation system to 10% (w/w). The ratio of inoculum to substrate was 1 to 4 in term of TS. The temperature during anaerobic digestion was set at 20, 38, 45 and 55^{o}C, respectively. All of anaerobic digestion tests were purged with N_2 for 5 min to remove oxygen in anaerobic digesters, and then sealed with butyl rubber stoppers immediately. In the whole process of anaerobic digestion, the experiments were shaken four times daily by hand in order to assure the sufficient mixing. All experiments were done in triplicate.

Struvite crystallisation. Struvite crystallisation was performed with the digested liquid harvested from anaerobic digestion by adding MgO slurry in 500-mL bottles. Aeration prior to struvite crystallization was conducted to raise the pH of the digested liquid as required for struvite crystallization (Jensen et al., 2016).

Analytical methods

TS, VS and P were measured according to American Public Health Association (Association, 1998). The volume of biogas produced during anaerobic digestion was periodically determined by the displacement of acidified (pH 2) and saturated NaCl solution, and a gas chromatography was employed to analyze the components of biogas (Zhan et al., 2013).The precipitated solid sample was analyzed using SEM. Dissolved Organic Matter (DOM) in the digested liquid was determined by a fluorescence spectrophotometer (F-7000, Hitachi, Japan) according the previous method (Chen et al. 2003).

RESULTS AND DISCUSSION

Effect of temperature on the production of biogas during anaerobic digestion

Figure 2 showed the effect of temperature on the production rate and yield of biogas during the whole anaerobic digestion. WAS exhibited a methanogenic pattern including fast biogas production phase, relatively stable phase and final phase through the whole experimental period no matter which temperature was. The production rate of biogas significantly increased with the increasing of temperature form 20 to 45^{o}C, but decreased subsequently with a further increase of temperature. At a temperature of 45^{o}C, the final biogas yield was 3.09 times higher than those at 38^{o}C, while 1.61 times higher than those at 55^{o}C. At 20^{o}C, the final yield of biogas was the poorest, resulted from the poor hydrolysis of organic substance in WAS in low temperature (Chae et al., 2008). The final biogas yields of 66, 205, 632 and 393 mL/g-VS were obtained at 20, 38, 45 and 55^{o}C, respectively. Temperature can improve the hydrolysis of complex organic substance to simple soluble substance. Therefore, a suitable temperature has a positive impact on the production of biogas (Deng et al., 2016). The results in this study showed that the optimal digestion temperature was 45^{o}C for the production of biogas. However, Lin et al. (2016) found that operating digestion temperature at 50^{o}C could give the maximum value of total biogas production from swine manure compared with other temperatures. The different substrates (WAS and swine manure) might be the main reason.

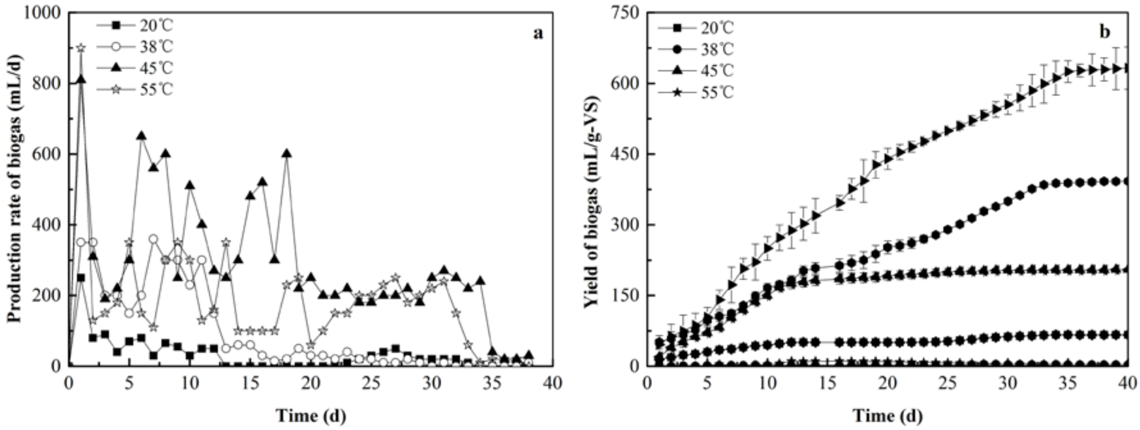

Figure 2. Variation of biogas production during anaerobic digestion at 20, 38, 45 and 55^oC (a: the production ratio of biogas; b: the yield of biogas).

The effect of temperature on the mean contents of CH_4, CO_2 and H_2 in the produced biogas during the relatively stable phase was shown in Figure 3. The mean content of biomethane increased with increasing digestion temperature from 20 to 45^oC. The results were in agreement with the previous studies (Chae et al., 2008). At 55^oC, the mean content of methane was similar to that at 45^oC. Contrarily, the mean meant of CO_2 in the produced biogas decreased with increasing digestion temperature.

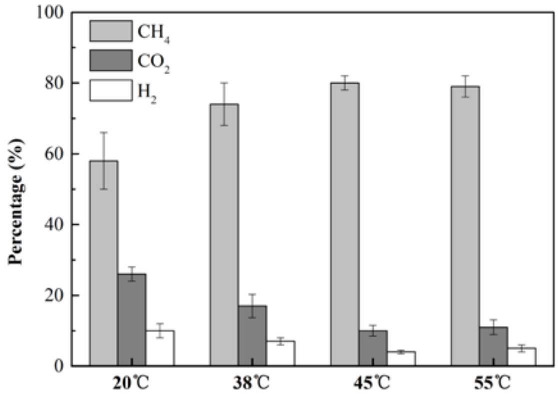

Figure 3. The mean contents of CH_4, CO_2 and H_2 in the produced biogas at 20, 38, 45 and 55^oC.

Effect of temperature on the production of PO_4^{3-}-P during anaerobic digestion

The effect of temperature on the concentration of PO_4^{3-}-P and soluble total P during the whole anaerobic digestion of 38 d was showed in Figure 4. Although the concentration of PO_4^{3-}-P increased rapidly at the beginning of anaerobic digestion, the value displayed a fluctuation during the subsequent anaerobic digestion, and even decreased gradually at the end of anaerobic digestion. This might because organic-P in WAS was no longer released in the form of PO_4^{3-}-P, and meanwhile PO_4^{3-}-P was shifted into other forms of P (Martí et al., 2010). The maximum concentration of PO_4^{3-}-P (114.1 mg/L) was found at the 9th day under the condition of 20^oC, suggesting that the low-temperature digestion might be suitable for the formation of PO_4^{3-}-P. The concentration of PO_4^{3-}-P reached the highest level at 20^oC, but the yield of biogas only arrived at 43 mL/g-VS that accounted for 65% of the total biogas yield (Figure 2b). Similar results were found for the other temperatures. The struvite crystallisation method of recovery phosphorus is limited by the availability of PO_4^{3-}-P (Jin et al., 2009). Therefore, in order to ensure the recover efficiency of biogas and phosphorus, a suitable digestion time of WAS for each temperature should be considered. In the case that 90% of the total biogas yield was obtained, digestion time of 29, 16, 31 and 31 d were chosen at 20, 38, 45 and 55^{o}C, respectively; under these conditions, the concentrations of PO_4^{3-}-P respectively reached 85.0, 72.2, 92.9 and 82.8 mg/L, with the biogas yields of 61, 185, 569 and 363 mL/g-VS. The variations of soluble total P during the whole anaerobic digestion at different temperatures were similar to PO_4^{3-}-P, which indicated that PO_4^{3-}-P was the main form of soluble P.

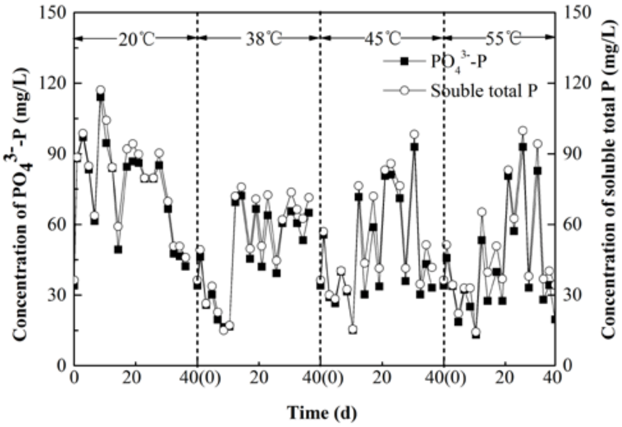

Figure 4. Variation of the concentrations of PO_4^{3-}-P and soluble total P during anaerobic digestion at the digestion temperature of 20, 38, 45 and 55^{o}C.

Performance of struvite crystallisation

The digested liquid separated from anaerobic digestion was used to recover phosphorus by the struvite precipitation method. Variations of the PO_4^{3-}-P concentration and the recovery ratio of soluble total P in the whole process of struvite crystallisation were shown in Figure 5. The concentration of PO_4^{3-}-P decreased rapidly within the first 2 hr, and then became slowly up to a gradually equilibrium in 12 hr. Although the concentrations of PO_4^{3-}-P for all of the digested liquid samples were varied with the similar trends, obvious differences in the recovery ratio of soluble total P were observed, as shown in Figure 5b. The recovery ratio of soluble total P for the digested liquid sample harvested at the digestion temperature of 45^{o}C was the highest, which reached 92.9%; while the recovery ratios of 76.5%, 84.3% and 87.5% were obtained at the digestion temperature of 20, 38 and 55^{o}C, respectively.

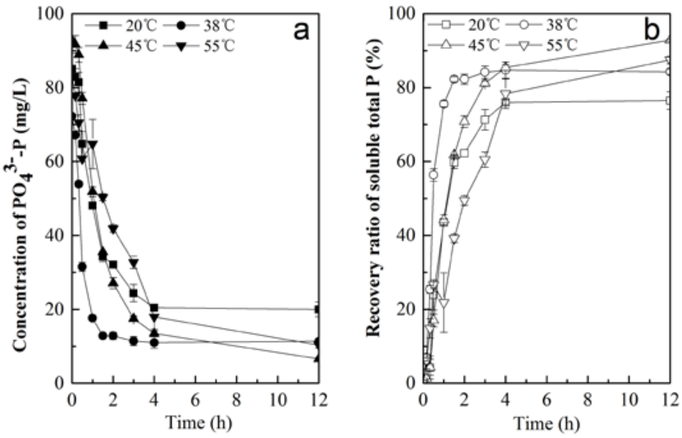

Figure 5. Variations of the PO_4^{3-}-P concentration and the recovery ratio of soluble total P during struvite crystallisation (a: concentration of PO_4^{3-}-P; b: recovery ratio of soluble total P).

Struvite is a white crystalline substance that consists of magnesium, nitrogen and phosphorus in equal molar concentrations (Guadie et al., 2014). The morphologies of struvite crystal include frustum of pyramid shaped, prismatic type, coffin shaped, feather shaped, needle type, etc (Chauhan et al., 2013; Guadie et al., 2014). It has been proved that struvite crystals with different morphologies were resulted from different growth parameters (Chauhan et al., 2013). The images of SEM in Figure 6 showed the morphologies of precipitate products formed in different digestion liquid samples. The precipitate products were all in white, and the crystals produced in this study were further confirmed as struvite according to the results of SEM analysis. Most of crystals particles retained prismatic or frustum of pyramid shape as observed in other studies (Zhou et al., 2015; Liu et al., 2016). However, the produced crystal quality was different for the different digestion liquid samples. When the liquid sample was from the digestion temperature of 45^{o}C, lots of regular and large crystals were formed in this sample with high crystal quality (Figure 6c). As for the other samples, more small particles were observed, and the surfaces of some crystal products were loose, especially for the sample from the digestion temperature of 20^{o}C (Figure 6a). It might be because the main components in the digestion liquid samples like dissolved organic matter (DOM) were different (Guadie et al., 2014).

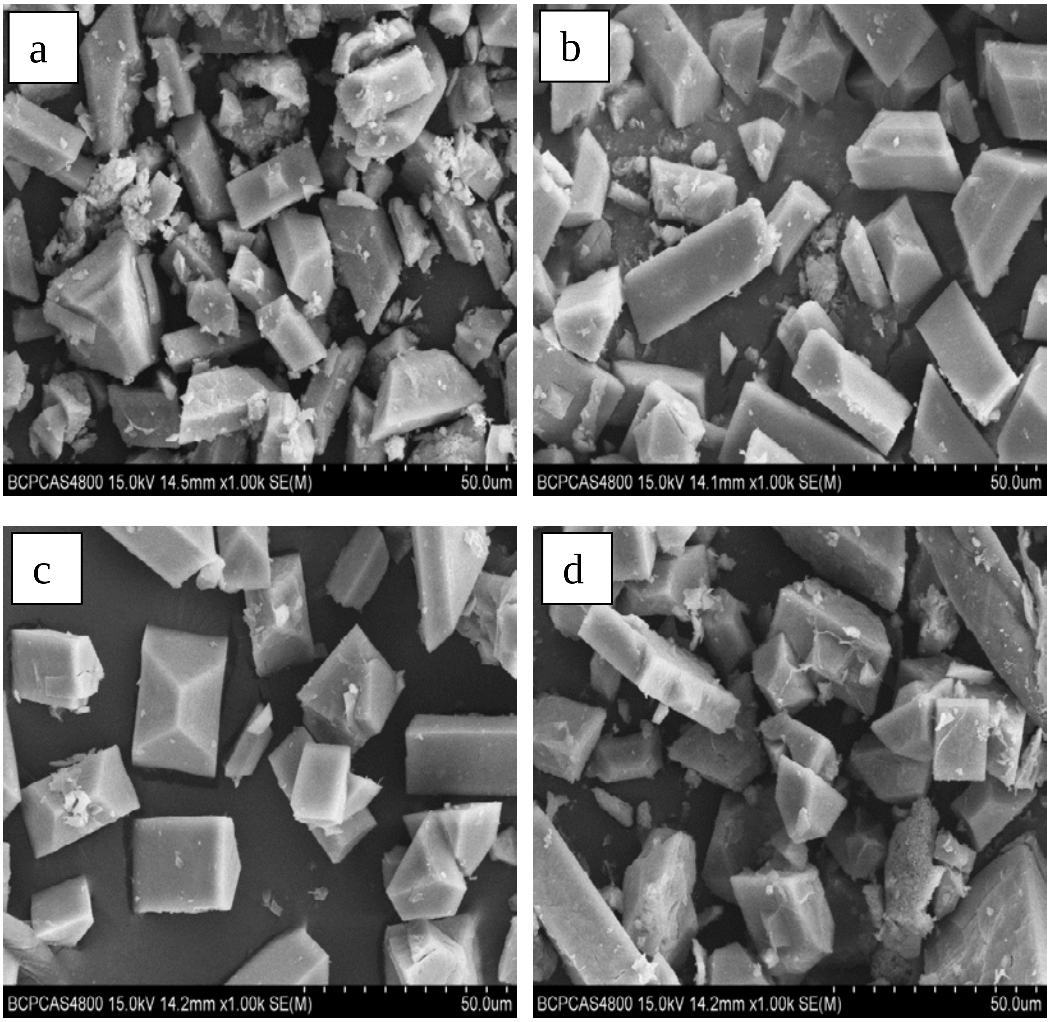

Figure 6. Scanning electron microscope (SEM) image of precipitate products from different samples at various digestion temperature (a: 20^{o}C; b: 38^{o}C; c: 45^{o}C; d: 55^{o}C).

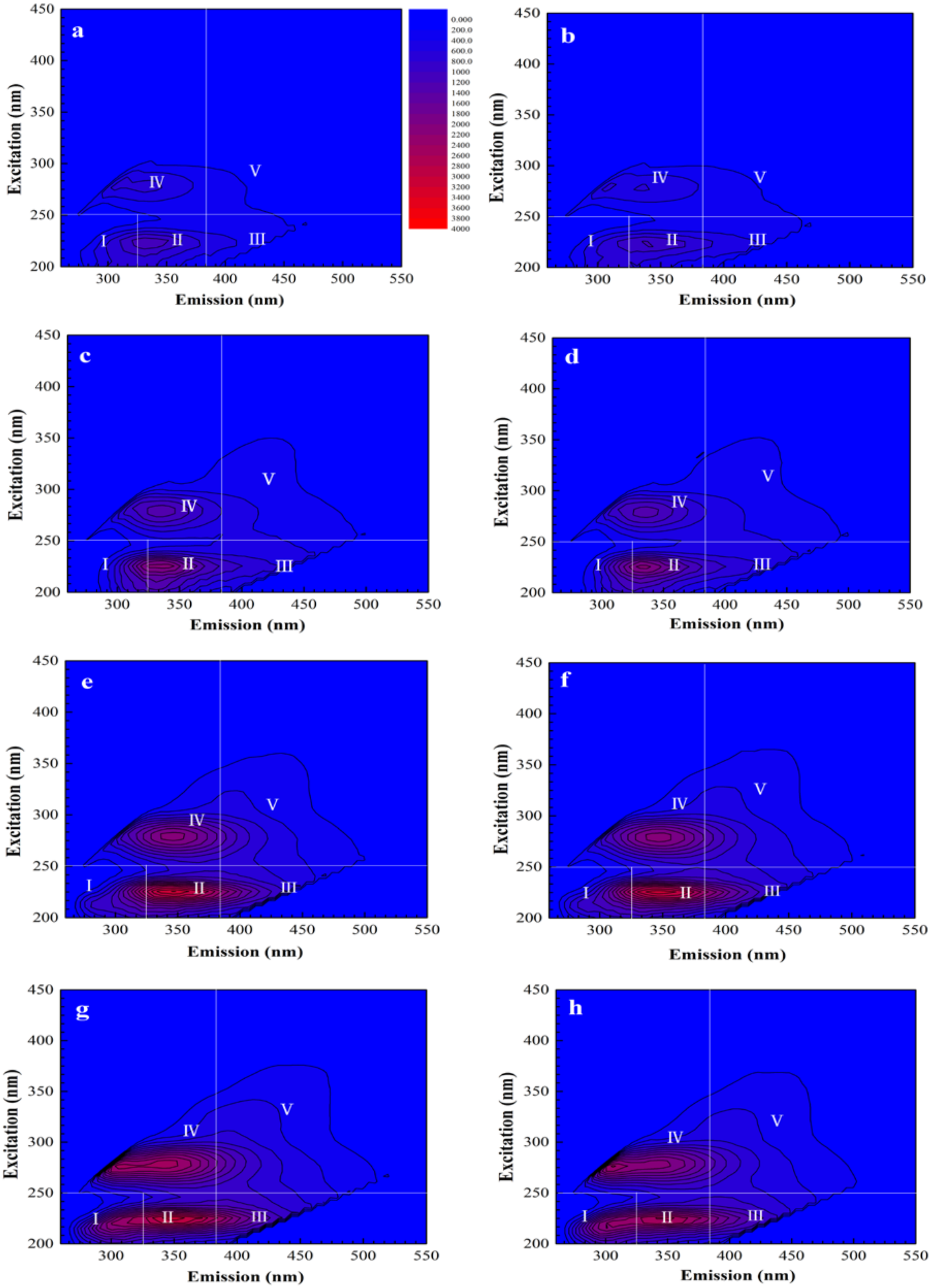

Figure 7. Excitation emission matrix analysis of dissolved organic matter for different samples (a: before crystallisation at digestion temperature of 20°C; b: after crystallisation at digestion temperature of 20°C; c: before crystallisation at digestion temperature of 38°C; c: after crystallisation at digestion temperature of 38°C; d: before crystallisation at digestion temperature of 45°C; e: after crystallisation at digestion temperature of 45°C; g: before crystallisation at digestion temperature of 55°C; h: after crystallisation at digestion temperature of 55°C).

Figure 7 presented the excitation emission matrix analysis of DOM in the samples before and after struvite crystallisation. The major excitation and emission wavelengths were the same for all of samples. Two significant peaks were observed, as shown in Figure 6. One was located in region II, the other was found in region IV. These two significant peaks were both related to soluble proteins (Chen et al. 2003; Liu et al., 2015). This indicated that proteins were the main soluble organic in digestion liquid samples from anaerobic digestion process of WAS, which was corroborated with our previous report (Liu et al., 2015). After the crystallization, the intensities of these two peaks became relatively weak, suggesting that some of soluble proteins were precipitated along with the crystallization process. Except the intensity, the fluorescence peak showed little changes, indicating that the struvite reaction crystallization process had no significant impact on DOM.

An integrated approach to biogas production and phosphorus recovery

According to the results of the biogas production and PO_4^{3-}-P concentration during the whole anaerobic digestion (Figure 2 and 4), the suitable digestion time under the different conditions of temperatures were confirmed; that is to say, digestion time of 29, 16, 31 and 31d were chosen at 20, 38,45 and 55°C, respectively. Recovery efficiencies of biogas and phosphorus after anaerobic digestion of 29 (20°C), 16 (38°C), 31 (45°C) and 31d (55°C) were compared, as shown in Table 2. Digestion temperature obviously played a significant role in the yield of biogas and the concentration of phosphors. The final yields of biogas under the different conditions of temperature were 61±4 mL/g-VS (20°C), 185±11 mL/g-VS (38°C), 569±27 mL/g-VS (45°C) and 363±6 mL/g-VS (55°C), respectively; simultaneously, the concentrations of PO_4^{3-}-P were separately corresponding to 85.0±1.4 mg/L, 72.2±1.2 mg/L, 92.9±2.5 mg/L and 82.8±2.5 mg/L. The maximum values of the biomethane yield and the recovery ratio of soluble total P were both achieved at the digestion temperature of 45°C; and they respectively reached 398±19 mL/g-VS and 92.9±0.3% with 41.4% reduction of total solids and 51.9% reduction of total volatile solids after 31d of anaerobic digestion.

Table 2. Recovery efficiency of biogas and phosphorus.

Items	Temperature			
	20°C	38°C	45°C	55°C
Biogas yield (mL/g-VS)	61 ± 4	185 ± 11	569 ± 27	363 ± 6
Biomethane yield (mL/g-VS)	31 ± 3	128 ± 10	398 ± 19	261 ± 12
Soluble total P concentration after anaerobic digestion (mg/L)	90.4 ± 4.3	75.9 ± 1.9	98.3 ±2.0	94.3 ± 5.1
PO_4^{3-}-P concentration after anaerobic digestion(mg/L)	85.0 ± 1.4	72.2 ± 1.2	92.9 ± 2.5	82.8 ± 2.5
PO_4^{3-}-P concentration after struvite crystallisation (mg/L)	19.9 ± 2.0	11.3 ± 0.5	6.6 ± 0.3	10.3 ± 0.8
Recovery ratio of soluble total P (%)	76.5 ± 2.4	84.3 ± 0.7	92.9 ± 0.3	87.5 ± 1.0
Removal ratio of total solids after anaerobic digestion (%)	39.3	43.8	41.4	50.5
Removal ratio of volatile solids after anaerobic digestion (%)	26.7	43.5	51.9	60.3

CONCLUSIONS

The integrated approach to biogas production through anaerobic digestion and phosphorus recovery with the struvite precipitation method was an effective way to treat and reutilize WAS. The digestion temperature played an important role in the production of biogas and the concentration of

PO_4^{3-}-P. The maximum yield of biogas was achieved at 45°C, while for the concentration of PO_4^{3-}-P it was 20°C. SEM analysis revealed that the morphologies of struvite crystals particles were prismatic or frustum of pyramid shape. Compared with other temperature, more regular and large crystals were formed at the digestion temperature of 45°C, suggesting that 45°C was favorable for the growth of high crystal struvite. The maximum values of the biomethane yield and the recovery ratio of soluble total P were both achieved at the digestion temperature of 45°C; and they respectively reached 398 mL/g-VS and 92.9% with 41.4% reduction of total solids and 51.9% reduction of total volatile solids after 31d of anaerobic digestion.

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