Zero-valent iron enhanced anaerobic digestion of pre-concentrated domestic wastewater for bioenergy recovery: characteristics and mechanisms

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Abstract: Pre-concentrated domestic wastewater (PDWW) rich in organic matters can be a suitable substrate for anaerobic digestion (AD) towards holistic resource and bioenergy recovery. Micron zero-valent iron (ZVI) was applied in designed batch experiments during anaerobic treatment of PDWW to verify its roles in performance enhancement and associated mechanisms. In the selected range of food to microorganism (F/M) ratio, 0.5 gCOD/gMLVSS was most appropriate as biomethane production potential (BMP) of 0.275 L CH_4/gCOD was obtained. The optimal ZVI dosage at fixed F/M of 0.5 was 6 g/L, further enhancing the BMP by 15.2%. Furthermore, ZVI improved the hydrolysis process (producing more soluble organics) and regulated acidification process (affecting volatile fatty acids distribution). No obvious impact on acetoclastic and hydrogenotrophic methanogenesis processes was noted with ZVI addition. ZVI based AD of the PDWW is promising for promoting the practical application of advanced domestic wastewater treatment strategy (pre-concentration plus anaerobic digestion).

Keywords: zero-valent iron; anaerobic digestion; domestic wastewater; biochemical methane production; bioenergy recovery

1. Introduction

Wastewater treatment using conventional aerobic biological processes can solve the concerned environmental pollution issue by effectively removing various pollutants. However, large amount of non-renewable energy is consumed without serious consideration on recycling available resources in wastewater. Nowadays, increasing attention is thus paid to more sustainable alternatives for wastewater treatment such as anaerobic digestion (AD). The advantages of AD process over its aerobic counterpart are lower energy consumption, less sludge production and smaller process footprint as well as biogas generation (Li et al., 2016). It has been estimated that applying AD-oriented system can even realize net energy recovery for domestic wastewater treatment (McCarty et al., 2011). However, at psychrophilic or cold temperature conditions using low-strength domestic wastewater for direct AD is challenging, which is more applicable for treating industrial wastewater or solid wastes with high organics content (Ekama et al., 2007).

To realize effective AD of domestic wastewater, pre-concentration technology has gained extensive attention to capture organic matters from the wastewater. One of the promising wastewater pre-concentration processes is membrane filtration, including high-loaded membrane bioreactor (Akanyeti et al., 2010), ultrafiltration or microfiltration (Kimura et al., 2017), forward osmosis filtration (Ansari et al., 2018) and dynamic membrane filtration (Li et al., 2017). Membrane-based pre-concentration processes can separate wastewater into two parts, the concentrate containing sufficient organic carbon source and the filtrate rich in nutrients (nitrogen and phosphorus). With influent chemical oxygen demand (COD) of 270-520 mg/L, pre-concentrated domestic wastewater (PDWW) containing COD more than 2000 mg/L is expected to be an effective substrate for AD (Mezohegyi et al., 2012; Gao et al., 2018). However, PDWW generally showed an altered property compared to the raw wastewater, because SCOD only accounted for 5%-10% of the total COD in PDWW and substantial retention of nutrients, suspended particles and even salts was also noted, showing inhibition effects on biogas production in some cases due to ammonia and salt accumulation (Gao et al., 2019). In biochemical methane potential (BMP) batch tests, PDWW achieved by membrane filtration could reach the methane yield of 200 mLCH$_4$/g COD or even more (Xiong et al., 2019; Gao et al., 2019). The results illustrate that PDWW may be partially utilized by anaerobes, so methane production is substantially lower than 350 mLCH$_4$/g COD, which is the theoretical methane yield at standard conditions. Thus, how to enhance the methane production of PDWW should be concerned, as little attention has been paid to the application feasibility of PDWW in AD process.

As documented, the membrane pre-concentration showed preferred retention of particulate and colloidal organic matter (70% -90% of TCOD) in the concentrate (Akanyeti et al., 2010; Li et al., 2017; Gao et al., 2018), while challenging the bio-methanation process due to low organics conversion rates. Though some pretreatment measures, such as thermal, chemical and mechanical methods (Zhen et al., 2017), have been proposed for improving AD process for organic wastes, however high energy consumption or chemical inputs made them costly (Wei et al., 2018) and reduced effectiveness to treat organic substrates with high water content (like the PDWW) might limit their applications. Recently, zero-valent iron (ZVI) has attracted increasing attention to degrade organic pollutants (Wang et al., 2009; He et al., 2015) and enhance methane generation during AD (Wei et al., 2018), due to its low input energy compared with other techniques. ZVI can play important roles in enhancing AD performance with major reasons listed as follows: (1) ZVI affects solution chemistry and anaerobic environment by regulating pH and ORP that promotes methanogenesis (Carpenter et al., 2015); (2) ZVI can effectively accelerate the hydrolysis–acidification process (Feng et al., 2014), and higher propionate conversion rate is also noted after ZVI addition (Meng et al., 2013); (3) adding ZVI can alter the microbial community structure evidenced by enriched syntrophic-methanogenic associations (Pan et al., 2019).

Furthermore, ZVI enhancing methane production was observed for diverse substrates at varied dosage. It was pointed out the methane yield of excess sludge increased by 131.6% in the presence of microscale ZVI with the dosage of 10 g/L (Yu et al., 2016). When 20 g/L of ZVI added to pig manure, methane yield was enhanced by 20% (Liang et al., 2017). Dosing 12 g/L of ZVI also enhanced methane yield of municipal solid waste by 41.7% (Kong et al., 2018). It is recognized that within the suitable dosage range ZVI plays positive roles in anaerobic degradation of organic wastes. However, limited investigation has been conducted for PDWW treatment, thus it is of great interest to verify the influence of ZVI on methane production of PDWW and also the potential mechanisms.

Therefore, in this study the objectives are: (1) to examine the methane production potential of PDWW at varied F/M ratios; (2) to investigate the effect of ZVI addition on enhancing methane production of PDWW; (3) to clarify the major mechanisms involved. Bath tests, including BMP and specific methanogenic activity (SMA), were conducted with some critical parameters determined, including the biogas production and composition, soluble chemical oxygen demand as well as volatile fatty acids. To date, quite limited investigations have been done to verify the effect of ZVI on anaerobic digestion of pre-concentrated domestic wastewater. The results will provide a better understanding of ZVI-based anaerobic wastewater treatment process towards bioenergy and resource recovery.

2. Materials and methods

2.1 Zero-valent iron

The ZVI in micron size (purity >98%, 100 mesh) purchased from Aladdin Corp., China was used in the experiments. High purity nitrogen gas has been used to protect the ZVI (sealed in bottles) from contact with air.

2.2. Substrate and seed sludge

The substrates (PDWW) used for a series of batch experiments (except methanogenic process) during anaerobic digestion were the concentrate of real domestic wastewater. As for examining the effect of adding ZVI on methanogenic process, synthetic substrates were applied, including various VFAs and H_2/CO_2 with details shown in Section 2.3.4. In this work, the designed batch tests included the influence of food to microorganism (F/M) ratio, the selection of appropriate ZVI dosage to enhance methane production as well as the effect of adding ZVI on the hydrolysis, acidification and methanogenic processes. The PDWW was obtained from a dynamic membrane filtration (DMF) reactor with the raw wastewater collected from a wastewater treatment plant as described elsewhere (Xiong et al., 2019). The quality of the PDWW is summarized in Table 1. Although the COD and SCOD of tested substrates showed some fluctuations, the ratios of SCOD to COD are between 9% and 17%, while the ratios of volatile solids (VS) to total solids (TS) are between 72% and 77%. In addition, PDWW contains a substantial amount of soluble proteins (52.72±10.95 mg/L) and polysaccharides (8.48±4.74 mg/L).

Table 1

Seed sludge used in the experiments was obtained from a local full-scale mesophilic anaerobic digester (Yang et al., 2020). The TS and VS of seed sludge used in all tests were 11.09 ± 0.89 g/L and 3.44 ± 0.43 g/L, respectively.

2.3. Design of batch experiments

2.3.1. Influence of F/M ratio on AD of the PDWW

To examine the effect of F/M ratio (gCOD/gMLVSS) on anaerobic digestion of PDWW, 20 mL seed sludge and certain amount of substate (PDWW) were added into 120 mL serum bottles with a working volume of 80 mL by diluting with deionized water if necessary, and the F/M ratios of 0.2, 0.5, 0.8 and 1.0 were chosen according to the preliminary experiments with F/M ratios ranging from 0.2 to 1.8. Blank control was conducted using deionized water to replace the substrate with other conditions the same as aforementioned. Duplicate tests were conducted for each F/M condition. All of the bottles were sealed and then purged with high purity nitrogen gas according to previous study (Yang et al., 2020). Afterwards, the bottles were placed in a water bath device under continuous shaking speed of 120 rpm at mesophilic temperature (35 °C).

2.3.2. Influence of ZVI dosage on AD of the PDWW

After the determination of the optimal F/M ratio in the previous section, batch tests were adopted to examine the influence of ZVI dosage on anaerobic digestion at the optimal F/M ratio of 0.5. The ZVI was directly added into serum bottles (120 mL) at the dosages of 0, 2, 4, 6 and 8 g/L. Before starting batch tests, the same pre-treatment procedures including sealing and nitrogen gas flushing were conducted. Other operational conditions were the same as described in Section 2.3.1.

2.3.3. Influence of ZVI on hydrolysis-acidification of the PDWW

In order to further explore the mechanisms of ZVI addition enhancing AD process, the influences of ZVI on the hydrolysis-acidification process were firstly investigated under well-controlled experiments. To ensure the AD process terminated at hydrolysis-acidification stage, a methanogenic inhibitor, sodium 2-bromoethanesulfonte ($C_2H_4BrO_3S$, BES), was used to inhibit methanogenic process at a BES concentration of 50 mmol/L (Lu et al., 2018).

The detailed design of batch experiments is shown in Table 2. Specifically, two sets of batch experiments were carried out based on with or without BES addition. Each set covered three groups of batch test, namely negative control group (with seed sludge addition only), positive control group (with seed sludge and substrate addition), and ZVI addition group (with seed sludge, substrate and 6 g/L ZVI addition). 60 mL of seed sludge was added into anaerobic bottles with total working volume of 210 mL (replenished by deionized water if necessary). Duplicate tests were done for each condition. The pre-treatment methods and operation conditions were the same as those mentioned in Section 2.3.1.

Table 2

2.3.4. Influence of ZVI on methanogenisis of the PDWW

To explore the effects of ZVI on acetoclastic methanogenesis and hydrogenotrophic methanogenesis processes, two kinds of substrate were adopted, namely, volatile fatty acids (VFAs) and H_2/CO_2 (Zhao et al., 2018). The VFAs used as the substrate were further divided into three categories: acetic acid alone, propionic acid alone, as well as a mixture containing acetic acid and propionic acid (COD ratio of 5: 1). Various VFAs (at fixed F/M=0.5), 6 g/L ZVI and 20 mL seed sludge were added into 120 mL anaerobic bottles (80 mL effective volume). As for experiment utilizing H_2 and CO_2

as the substrates, 20 mL seed sludge and 6 g/L ZVI were put into the anaerobic bottle, then the bottle was purged with the hydrogen and carbon dioxide gas mixture (volume ratio of 8: 2) for 5 min. The gas component was measured every 2 h and then filled 40 mL mixed gas into the bottles to keep the 1.4 times of standard atmospheric pressure. Blank control was conducted without ZVI addition, and duplicate tests were carried out.

2.4. Data analysis

Batch tests results regarding the impact of ZVI on the methanogenic process were simulated by the modified Gompertz equation (Eq. (1)) using Origin 8.0 software (Origin Cop., USA).

$$P = P_0 \cdot exp\left\{ -exp\frac{R_{max} \cdot e}{P_0} \cdot \left[(t_0 - t) + 1 \right] \right\} \qquad (1)$$

Where P is cumulative methane production (mL CH_4/gCOD), P_0 is the maximum potential of methane production (mL CH_4/gCOD), R_{max} is the maximum methane production rate (mL CH_4/gCOD·d), e=2.7183, t_0 is the lag time (day) and t is the cultivation time (day).

2.5. Analytical methods

Biogas production was tested manually by using a glass syringe, and biogas composition (mainly CH_4, CO_2, H_2 and N_2) was detected using a gas chromatograph (GC) (GC7900, Tianmei, China) (Yang et al., 2020). To analyze the content of VFAs and lactate acid, a liquid chromatograph (LC-20A, Shimadzu, Japan) was used, which was equipped with an ultraviolet detector and a column (Aminex HPX–87H Column, Bio-Rad, USA). The mobile phase was 0.05 mol/L sulfuric acid buffer liquid at a flow velocity of 0.3 mL/min. The detector temperature was set at 40 °C with UV wavelength of 210 nm. The modified Lowry method was used to measure proteins (Lowry et al, 1951), and Anthrone-sulfuric acid method was adopted to measure polysaccharides (Gaudy et al, 1962). Measurements for SCOD, COD, TS and VS were based on the standard methods (APHA, 1998).

3. Results and discussion

3.1. Effect of F/M ratio on anaerobic digestion of PDWW

The effect of F/M ratio (0.2-1.0) on accumulative methane production using PDWW as the substrate is shown in Fig. 1(a) according to batch BMP tests lasting for 36 d, with the final cumulative methane production presented in Fig. 1(b). The maximum cumulative methane production reached 0.275 L CH_4/gCOD at F/M ratio of 0.5, while the values were 0.265, 0.266 and 0.263 L CH_4/gCOD when the F/M ratios were 0.2, 0.8 and 1.0. Thus, F/M ratio of 0.5 is considered to be optimal for anaerobic digestion of PDWW at least under the test conditions applied. However, the accumulative methane production of PDWW was approximately 0.26-0.28 L CH_4/gCOD when the F/M ranged from 0.5 to 1.0, still lower than theoretical methane yield. On the other hand, the reported methane yields during anaerobic treatment of real domestic wastewater were from 0.13 to 0.27 L CH_4/gCOD (Ozgun et al., 2013; Gouveia et al., 2015). It meant that methane production seemed to be unaffected after pre-concentration treatment of domestic wastewater. Besides, compared with reported BMP values of sewage sludge (0.18-0.21 L CH_4/gCOD) (Ding et al., 2017), PDWW showed higher methane production potential.

It has been reported that the duration for biogas production to be stable in BMP tests was less than 15 d when using food waste, sewage sludge and maize as the substrates (Koch et al., 2017; Zhang et al., 2007). However, the duration using PDWW as the substrate was between 17 and 23 d. Anaerobic digestion of PDWW appeared to be slower, possibly due to the difference in composition between organic solid wastes and PDWW. The SCOD/COD of PDWW used was 9.2%, illustrating that high content of particulate organic matters existed in PDWW, therefore AD process might be limited at the hydrolysis stage. Overall, the results indicated that PDWW is suitable for methane production and the most appropriate F/M ratio is 0.5, though the methane production needs to be improved and the duration of AD process should be reduced.

Fig. 1.

3.2. Effect of ZVI dosage on anaerobic digestion of PDWW

To verify the effect of ZVI addition on AD of the PDWW, batch experiments results at F/M ratio of 0.5 lasting for 20 d with a series of ZVI dosage are shown in Fig. 2(a). Firstly, the final accumulative methane production of the control is 0.254 L CH_4/g COD, which reaches 72.6% of the theoretical methane production and is approximately equal to VS/TS ratio (72.9%) of the substrate used in batch tests. It is supposed that the available organics in PDWW for methane production is related to the content of volatile organic substances.

Compared with the control, BMP in the test group with 6 g/L ZVI addition was increased by 15.2%, while BMP was improved by 10.6%, 10.4% and 9.7% with 2, 4 and 8 g/L of ZVI addition (Fig. 2(b)). Therefore, the most appropriate dosage of ZVI enhancing methane production was regarded as 6 g/L at F/M of 0.5. It has been reported that simulated brewery wastewater exposed to ZVI showed a methane production increasing rate ranging from 5% to 28.3% (Carpenter et al., 2015). In other studies, ZVI has enhanced methane production by at least 20% using sewage sludge as the substrate (Hu et al., 2019; Wei et al., 2018). Thus, how methane production of PDWW was enhanced by ZVI addition deserves further investigation to clarify the underlying mechanisms.

Furthermore, it is not the fact that the higher the ZVI dosage is, the better the methane production performance will be. ZVI can release of H_2 and OH^- in anaerobic conditions as expressed by the following equation (Eq. (2)).

$$Fe+2H_2O \rightarrow Fe^{2+}+H_2+2OH^- \qquad (2)$$

Consequently, why the high dosage of ZVI may inhibit methanogenesis can be explained as follows. High H_2 partial pressures due to rapid H_2 production at excess ZVI addition will lead to several negative effects on methanogenesis process (Yang et al., 2013). For instance, high partial pressures of H_2 bring about CO production ($CH_3COO^-+H^++H_2 \rightarrow CH_4+CO+H_2O$ $\Delta G'^{\theta}$=-15.8kJ/mol) breaking the balance among CH_4, CO_2, and CO thus inhibiting acetoclastic methanogenesis (Zinder et al., 1992). Moreover, high hydrogen partial pressure also makes the methanogenic process thermodynamically unfavorable (Yang et al., 2013). On the other hand, strong reduction action of ZVI is harmful to bacteria and methanogens extremely by decomposing functional groups of proteins on cell membranes and destructing respiration occurring on the surface of the cell membranes (Xu et al., 2019).

Fig. 2.

3.3. Effect of ZVI on hydrolysis-acidification process during AD

3.3.1. Effect of ZVI on hydrolysis process

During hydrolysis stage (the first and commonly rate-limiting stage of AD process), complex organic substances were decomposed into monosaccharides and disaccharides, amino acids, peptides and others under the action of extracellular hydrolase of hydrolytic bacteria. SCOD chosen as an indicator was measured to investigate the influence of ZVI on PDWW hydrolysis process.

Substrates were hydrolyzed and eventually converted into methane in the two groups without BES (methanogenic inhibitor) as mentioned in Section 2.3. As shown in Fig. 3(a), SCOD in both tests groups without BES addition (positive control without ZVI addition, the other with 6 g/L ZVI addition) showed an increasing trend firstly (within 12 h) and then decreased to around or below 30 mg/L. It was presumed that easily biodegradable organics in the substrate were substantially hydrolyzed (within 12 h), causing the rate of hydrolysis process higher than the rate of methanogenesis process, thus SCOD concentrations increased at the initial stage. However, along with limited available organics being degraded, the rate of hydrolysis process gradually reduced, causing SCOD concentrations to be reduced and stable. Compared with the positive control, ZVI addition group showed the largest SCOD increment of 51.88 mg/L at 12 h, and also presented higher SCOD continuously during the remaining cultivation time. It is preliminarily verified that ZVI promotes the hydrolysis process during anaerobic digestion of PDWW.

Fig. 3.

On the other hand, when BES is used for preventing methane production SCOD will not be consumed for methanogenesis, but accumulated or converted as metabolic products (such as VFAs). Accumulative SCOD is measured and shown in Fig. 3(b). Similarly, the largest increment in SCOD of 44.34 mg/L at 12 h was noted for ZVI addition group compared to the control group. In addition, in both groups SCOD gradually increased with the fermentation time, while ZVI addition group always showed higher SCOD (33 mg/L after 120 h) than the control one. The results further verified that ZVI addition accelerated the hydrolysis process. It is mainly because ZVI as an electron donor promotes the breaking of unsaturated chemical bonds of organic substances in the hydrolysis stage. Moreover, iron is a necessary element for synthesizing related enzymes to fulfil extracellular hydrolysis process (Yang et al., 2013).

3.3.2. Effect of ZVI on acidification process

To investigate ZVI addition affecting acidification process (including acidogenesis and acetogenesis), the accumulation and behaviors of VFAs (mainly acetic acid) and lactic acid were analyzed since in the continuous anaerobic fermentation stage acidogenic and acetogenic processes can not be completely separated. In tested groups without BES addition VFAs and lactic acid were not accumulated with the total contents all below 15 mg/L due to their continuous conversion to biogas by the methanogens. As for the tested groups with BES addition, hydrolyzed organics are supposed to mainly convert into VFAs rather than methane production. The distribution of VFAs and lactic acid with time in three groups (negative control with BES addition, positive control with BES addition and 6g/L ZVI addition) is shown in Fig. 4. The results of the positive control group (Fig. 4(b)) showed that acetic acid was the major product during PDWW acidification stage, with acetic acid accounting for more than 70% of the total products followed by other VFAs and lactic acid. Similar results regarding total VFAs content were noted for 6 g/L ZVI addition group (Fig. 4(c)). It was indicated that adding ZVI seemed to show little impact on the acidogenesis process as a similar level of organic acids accumulation was obtained. However, a minor difference in VFA distribution was noted as lactic acid content in ZVI addition group was lower than that in the positive control, showing potential impact on acetogenesis processes by regulating acetic acid production from other VFAs. This phenomenon was in agreement with previous studies reporting enhanced propionic and butyric acids conversion to acetic acid by ZVI addition (Meng et al., 2013; Kong et al., 2018).

Furthermore, it is well known that acetic acid can be directly used by acetoclastic methanogens for methane production. Therefore, the obtained results indicated that PDWW was a suitable substrate due to the high proportion of acetic acid. But a substantial accumulation of propionic acid followed by butyric acid and isovaleric acid was also noted. Propionic acid accounts for around 10% of the final fermentation products since it has been reported that protein-containing wastewater is prone to produce propionic acid.

$$CH_3CH_2COO^- + 3H_2O \rightarrow CH_3COO^- + HCO_3^- + H^+ + 3H_2 \quad \Delta G'^{\theta} = +76.1\ kJ/mol \quad (3)$$

$$CH_3CH_2\,CH_2COO^- + 2H_2O \rightarrow 2CH_3COO^- + H^+ + 2H_2 \quad \Delta G'^{\theta} = +48.1\ kJ/mol \quad (4)$$

$$CH_3CHOHCOO^- + 2H_2O \rightarrow CH_3COO^- + HCO_3^- + H^+ + 2H_2 \quad \Delta G'^{\theta} = -4.2\ kJ/mol \quad (5)$$

As shown in Eqs. (3) and (4), the production of hydrogen and acetic acid from propionic acid and butyric acid cannot proceed spontaneously under standard conditions, unless at low partial pressure of H_2 (less than 10 Pa) with the actual free energy less than 0. Generation of acetic acid from lactic acid (Eq. (5)) seemed to be not easily proceeded as well. Moreover, approximate 30% of propionic acid and other VFAs existing in PDWW fermentation products is responsible for low methane production rate using PDWW as the substrate, possibly limited by the low conversion rate of these VFAs to acetic acid even with ZVI addition (Huang et al., 2019).

Fig. 4.

3.4. Effect of ZVI on methanogenesis process during AD

3.4.1. Effect of ZVI on acetoclastic methanogenesis process

Generally, it is recognized that in anaerobic digestion methane produced by acetoclastic methanogenesis process (acetic acid as the substrate) accounts for 70%, with the rest attributed to hydrogenotrophic methanogenesis process (H_2/CO_2 as the substrate). Batch tests were conducted to explore the effects of ZVI on acetoclastic methanogenesis using various VFAs as the organic substrates, including acetic acid (Fig. 5(a)), propionic acid (Fig. 5(b)) and a mixture of acetic acid and propionic acid (Fig. 5(c)), The results regarding accumulative methane production were simulated by using Gompertz equation with detailed parameters presented in Table 3.

Although there were no obvious differences in methane production potential (P_0) and lag time (t_0), the maximum methane production rate (R_{max}) with 6g/L ZVI addition group was 6% greater than the positive control when the substrate was acetic acid. However, when the substrates were changed to propionic acid or the mixture of acetic acid and propionic acid, the methane production potential with 6 g/L ZVI addition group was 4%-6% lower than the positive control, while the maximum methane production rate with 6 g/L ZVI addition group was 7%-17% lower than the positive control. This can be explained that hydrogen production by ZVI dissolution (shown in Eq. (5)) will be thermodynamically detrimental for propionic acid conversion into acetic acid, and subsequently acetoclastic methanogenesis can be inhibited due to less available acetic acid (Capson-Tojo et al., 2017). However, the reduction of BMP with ZVI addition was insignificant, thus ZVI seemed to have no obvious effect on the acetoclastic methanogenesis process with the substrates dominated by acetic acid.

Fig. 5.

Table 3

3.4.2. Effect of ZVI on hydrogenotrophic methanogenesis process

As shown in Fig. 5(d), the effect of ZVI on hydrogenotrophic methanogenesis process is also investigated. It was noted that accumulative methane production increased linearly with batch test time, and the methanogenesis rate could be obtained accordingly. The hydrogenotrophic methanogenesis rates of positive control and 6 g/L ZVI addition group were 0.012 and 0.011 $LCH_4/gMLVSS·d$, indicating no enhancement of hydrogenotrophic methanogenesis by adding ZVI. It was different from one previous study reporting that methane production from hydrogenotrophic methanogenesis was approximately improved by 70% with ZVI addition (Zhao et al., 2018). In this work, the inoculums collected from a waste sludge treatment plant was used, and also it highlighted the importance of hydrogenotrophic methanogenesis and syntrophic methane production between syntrophic bacteria and methanogens enhanced by ZVI addition. Moreover, conducting fluorescence in situ hybridization (FISH) analysis indicated that adding waste iron scraps enhanced the abundance of acidifying bacteria, acetoclastic and hydrogenotrophic methanogens of the pre-cultured inoculum (Hao et al., 2017). The main reason might be that the activity of hydrogenotrophic methanogens in the seed sludge (from full-scale anaerobic digester treating industrial wastewater) was low, and also the inoculum was not acclimatized to the tested conditions (such as ZVI addition). Therefore, more efforts are suggested to verify this effect by using well-adapted inoculum in long-term operated anaerobic digesters. In addition, it will be of great interest to apply advanced analytical methods, such as high throughput sequencing and FISH, to provide more evidence for illuminating the exact effects of ZVI on microbial community properties.

3.5. Implications for practical application

Wastewater is increasingly recognized as a valuable resource rather than a waste, and this conceptual change has driven the shift of wastewater treatment paradigm from pollutant removal to maximum resource recovery. In this case, many exploration and practice have been made from varied aspects, such as proposing hypothetical treatment systems with future perspective (Verstraete et al., 2009; McCarty et al., 2011), evolving wastewater infrastructure paradigm based on sustainability principles (Wang et al., 2018), wastewater pretreatment for carbon capture or redirection (Sancho et al., 2019; Guven et al., 2019) as well as nutrients recovery (Yan et al., 2018). However, most of the current efforts are paid to system development and modelling, the actual conditions of resource recovery and potential technical limitations are insufficiently understood and to be well investigated.

This study primarily verified the promising strategy (membrane filtration for organics capture plus anaerobic digestion for bioenergy generation) for useful resource recovery. However, due to high enrichment of particulate and colloidal organic substances from domestic wastewater, the efficiency of AD process seemed to be easily limited, due to low reaction rate of the hydrolysis-acidification process (Zhen et al., 2017). The proposed measure of ZVI addition to enhance AD performance was investigated, showing substantial enhancement on the hydrolysis-acidification of pre-concentrated domestic wastewater and overall methane production. A rough comparative estimation on economic benefit between conventional AD and ZVI-assisted AD for PDWW treatment is carried out with some important default values based on one previous study (Wei et al., 2018). The initial conditions are set as follows: treatment capacity of anaerobic digester of 5,000 m^3/d, methane yield of 0.25 and 0.29 $LCH_4/gCOD$, and the produced biogas is considered to be combusted in a combined heat and power (CHP) system with the benefit from power generation firstly considered rather than heat production. The calculation results indicate that ZVI-based AD system can be more beneficial than its counterpart (AD alone) when taking power production benefit, ZVI cost and other expenditures (ZVI transportation and dosing) into comprehensive consideration. Furthermore, using low-cost ZVI (such as scrap iron) or optimizing ZVI usage, and considering phosphorous recovery and sulfur control during AD process will further increase the benefits by the enhanced methane production and resource recovery.

In all, the results obtained highlighted that further optimization of the AD process of PDWW is needed with the focuses on integrated low-cost pre-treatment method and the enhancement of ZVI utilization efficiency to realize the efficient recovery of renewable resource.

4. Conclusions

The viability of ZVI addition to improve PDWW treatment by AD process was investigated. The PDWW containing high content of particulate organics could be effectively digested at optimal F/M of 0.5 gCOD/gMLVSS while adding 6 g/L ZVI further enhanced the BMP by 15.2%. The major contribution of ZVI was attributed to substantially enhancing the hydrolysis process and regulating the acidification process rather than affecting methanogenesis process. The results indicate that integrating ZVI with pre-treatment measures to further enhance PDWW hydrolysis-acidification will be appreciated to realize the application of the proposed strategy (wastewater pre-concentration plus anaerobic digestion) towards holistic resource recovery.

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Appendix A. Supplementary data

E-supplementary data for this work can be found in e-version of this paper online.

References

[1] Akanyeti, I., Temmink, H., Remy, M., Zwijnenburg, A., 2010. Feasibility of bioflocculation in a high-loaded membrane bioreactor for improved energy recovery from sewage. Water Sci Technol, 61, 1433-1439.

[2] Ansari, A.J., Hai, F.I., Price, W.E., Ngo, H.H., Guo, W., Nghiem, L.D., 2018. Assessing the integration of forward osmosis and anaerobic digestion for simultaneous wastewater treatment and resource recovery. Bioresour. Technol. 260, 221-226.

[3] APHA., 1998. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington, DC.

[4] Capson-Tojo, G., Ruiz, D., Rouez, M., Crest, M., Steyer, J.P., Bernet, N., Delgenes, J.P., Escudie, R., 2017. Accumulation of propionic acid during consecutive batch anaerobic digestion of commercial food waste. Bioresour. Technol. 245, 724-733.

[5] Carpenter, A.W., Laughton, S.N., Wiesner, M.R., 2015. Enhanced Biogas Production from Nanoscale Zero Valent Iron-Amended Anaerobic Bioreactors. Environ. Eng. Sci. 32(8), 647-655.

[6] Ding, H.H., Chang, S., Liu, Y., 2017. Biological hydrolysis pretreatment on secondary sludge: Enhancement of anaerobic digestion and mechanism study. Bioresour. Technol. 244, 989-995.

[7] Ekama, G.A., Sotemann, S.W., Wentzel, M.C., 2007. Biodegradability of activated sludge organics under anaerobic conditions. Water Res. 41, 244-252.

[8] Feng, Y., Zhang, Y., Quan, X., Chen, S., 2014. Enhanced anaerobic digestion of waste activated sludge digestion by the addition of zero valent iron. Water Res. 52, 242-250.

[9] Fu, F., Dionysiou, D.D., Liu, H., 2014. The use of zero-valent iron for groundwater remediation and wastewater treatment: a review. J. Hazard. Mater. 267, 194-205.

[10]Gao, Y., Fang, Z., Liang, P., Huang, X., 2018. Direct concentration of municipal sewage by forward osmosis and membrane fouling behavior. Bioresour. Technol. 247, 730-735.

[11]Gao, Y., Fang, Z., Liang, P., Zhang, X., Qiu, Y., Kimura, K., Huang, X., 2019. Anaerobic digestion performance of concentrated municipal sewage by forward osmosis membrane: Focus on the impact of salt and ammonia nitrogen. Bioresour. Technol. 276, 204-210.

[12]Gaudy, A., 1962. Colorimetric determination of protein and carbohydrate. Ind. Water. Wastes 7, 17-22.

[13]Gouveia, J., Plaza, F., Garralon, G., Fdz-Polanco, F., Pena, M., 2015. A novel configuration for an anaerobic submerged membrane bioreactor (AnSMBR). Long-term treatment of municipal wastewater under psychrophilic conditions. Bioresour. Technol. 198, 510-519.

[14]Guven, H., Dereli,R.K., Ozgun, H., Ersahin, M. E., Ozturk, I., 2019. Towards sustainable and energy efficient municipal wastewater treatment by up-concentration of organics, Prog. Energ, Combust. 70, 145-168.

[15]Hao, X., Wei, J., van Loosdrecht, M.C.M., Cao, D., 2017. Analysing the mechanisms of sludge digestion enhanced by iron. Water Res. 117, 58-67

[16]He, Y.T., Wilson, J.T., Su, C., Wilkin, R.T., 2015. Review of Abiotic Degradation of Chlorinated Solvents by Reactive Iron Minerals in Aquifers. Ground Water Monit. R. 35(3), 57-75.

[17]Hu, Y., Wang, F., Lv, G., Chi, Y., 2019. Enhancing the Biogas Production of Sludge Anaerobic Digestion by a Combination of Zero-Valent Iron Foil and Persulfate. Energ. Fuel. 33(8), 7436-7442.

[18]Huang, J., Chen, S., Wu, W., Chen, H., Guo, K., Tang, J., Li, J., 2019. Insights into redox

mediator supplementation on enhanced volatile fatty acids production from waste activated sludge. Environ. Sci. Pollut. R. 26(26), 27052-27062.

[19]Kimura, K., Honoki, D., Sato, T., 2017. Effective physical cleaning and adequate membrane flux for direct membrane filtration (DMF) of municipal wastewater: Up-concentration of organic matter for efficient energy recovery. Sep. Purif. Technol. 181, 37-43.

[20]Koch, K., Lippert, T., Drewes, J.E., 2017. The role of inoculum's origin on the methane yield of different substrates in biochemical methane potential (BMP) tests. Bioresour. Technol. 243, 457-463.

[21]Kong, X., Yu, S., Xu, S., Fang, W., Liu, J., Li, H., 2018. Effect of Fe(0) addition on volatile fatty acids evolution on anaerobic digestion at high organic loading rates. Waste Manage. 71, 719-727.

[22]Li, S., Yang, Y., Hu, Y., Tang, J., Wang, X.C., 2017. Development of a novel two-stage powdered activated carbon-dynamic membrane filtration (PAC-DMF) system for direct physicochemical wastewater treatment. Desalin. Water Treat. 99, 299-308.

[23]Li, W.-W., Yu, H.-Q., 2016. Advances in Energy-Producing Anaerobic Biotechnologies for Municipal Wastewater Treatment. Engineering, 2(4), 438-446.

[24]Liang, Y.G., Li, X.J., Zhang, J., Zhang, L.G., Cheng, B., 2017. Effect of microscale ZVI/magnetite on methane production and bioavailability of heavy metals during anaerobic digestion of diluted pig manure. Environ. Sci. Pollut. R. 24(13), 12328-12337.

[25]Lowry, O.H., Rosebrough, N.J., Farr, A.L., Randall, R.J., 1951. Protein measurement with the Folin phenol reagent. J. Biol. Chem. 193, 265–275.

[26]Lu, X., Ni, J., Zhen, G., Kubota, K., Li, Y.-Y., 2018. Response of morphology and microbial community structure of granules to influent COD/SO_4^{2-} ratios in an upflow anaerobic sludge blanket (UASB) reactor treating starch wastewater. Bioresour. Technol. 256, 456-465.

[27]McCarty, P.L., Bae, J., Kim, J., 2011. Domestic wastewater treatment as a net energy producer – can this be achieved? Environ. Sci. Technol. 45, 7199-7106.

[28]Meng, X., Zhang, Y., Li, Q., Quan, X., 2013. Adding Fe^0 powder to enhance the anaerobic conversion of propionate to acetate. Biochem. Eng. J. 73, 80-85.

[29]Mezohegyi, G., Bilad, M.R., Vankelecom., Ivo F.J., 2012. Direct sewage up-concentration by submerged aerated and vibrated membranes. Bioresour. Technol. 118, 1-7.

[30]Ozgun, H., Dereli, R.K., Ersahin, M.E., Kinaci, C., Spanjers, H., van Lier., J.B., 2013. A review of anaerobic membrane bioreactors for municipal wastewater treatment: Integration options, limitations and expectations. Sep. Purif. Technol. 118, 89-104.

[31]Pan, X., L., N, Li, C., Ning, J., Wang, T., Wang, R., Zhou, M., Zhu., G., 2019. Impact of nano zero valent iron on tetracycline degradation and microbial community succession during anaerobic digestion. Chem. Eng. J. 359,662-671.

[32]Sancho, I., Lopez-Palau, S., Arespacochaga, N., Cortina, J.L., 2019. New concepts on carbon redirection in wastewater treatment plants: A review, Sci. Total Environ. 647, 1373-1384.

[33]Verstraete, W., Van de Caveye, P., Diamantis, V., 2009. Maximum use of resources present in domestic “used water”. Bioresour. Technol. 100, 5537-5545.

[34]Wang, S.M., Tseng, S.K., 2009. Dechlorination of trichloroethylene by immobilized autotrophic hydrogen-bacteria and zero-valent iron. J. Biosci. Bioeng. 107(3), 287-292.

[35]Wang, X., Daigger, G., Lee, D.-J., Liu, J., Ren, N.-Q., Qu, J., Liu, G., Butler, D. 2018. Evolving wastewater infrastructure paradigm to enhance harmony with nature. Sci. Adv. 4, eaaq0210.

[36]Wei, J., Hao, X., van Loosdrecht, M.C.M., Li, J., 2018. Feasibility analysis of anaerobic digestion of excess sludge enhanced by iron: A review. Renew. Sust. Energ. Rev. 89, 16-26.

[37]Wei, W., Cai, Z., Fu, J., Xie, G.-J., Li, A., Zhou, X., Ni, B.-J., Wang, D., Wang, Q., 2018. Zero valent iron enhances methane production from primary sludge in anaerobic digestion, Chem. Eng. J. 351, 1159-1165.

[38]Xiong, J., Yu, S., Hu, Y., Yang, Y., Wang, X.C., 2019. Applying a dynamic membrane filtration (DMF) process for domestic wastewater preconcentration: Organics recovery and bioenergy production potential analysis. Sci. Total Environ. 680, 35-43.

[39]Xu, R., Xu, S., Zhang, L., Florentino, A.P., Yang, Z., Liu, Y., 2019a. Impact of zero valent iron on blackwater anaerobic digestion. Bioresour. Technol. 285, 121351.

[40]Xu, X., Xing, S., Xu, M., Fu, P., Gao, T., Zhang, X., Zhao, Y., Zhao, C., 2019b. Highly sensitive and specific screening of EGFR mutation using a PNA microarray-based fluorometric assay based on rolling circle amplification and graphene oxide. RSC Advs. 9(66), 38298-38308.

[41]Yan, T., Ye, Y., Ma, H., Zhang, Y., Guo, W., Du, B., Wei, Q., Wei, D., Ngo H.H., 2018. A

critical review on membrane hybrid system for nutrient recovery from wastewater, Chem. Eng. J. 348, 143-156,

[42]Yang, Y., Guo, J., Hu, Z., 2013. Impact of nano zero valent iron (NZVI) on methanogenic activity and population dynamics in anaerobic digestion. Water Res. 47(17), 6790-6800.

[43]Yang, Y., Zang, Y., Hu, Y., Wang, X.C., Ngo, H.H. 2020. Upflow anaerobic dynamic membrane bioreactor (AnDMBR) for wastewater treatment at room temperature and short HRTs: Process characteristics and practical applicability. Chem. Eng. J. 383, 123186.

[44]Yu, B., Huang, X., Zhang, D., Lou, Z., Yuan, H., Zhu., N., 2016. Response of sludge fermentation liquid and microbial community to nano zero-valent iron exposure in a mesophilic anaerobic digestion system. RSC Adv. 6, 24236-24244.

[45]Zhang, R., El-Mashad, H.M., Hartman, K., Wang, F., Liu, G., Choate, C., Gamble, P., 2007. Characterization of food waste as feedstock for anaerobic digestion. Bioresour. Technol. 98(4), 929-935.

[46]Zhao, Z., Zhang, Y., Li, Y., Quan, X., Zhao, Z., 2018. Comparing the mechanisms of ZVI and Fe_3O_4 for promoting waste-activated sludge digestion. Water Res. 144, 126-133.

[47]Zhen, G., Lu, X., Kato, H., Zhao, Y., Li, Y.-Y., 2017. Overview of pretreatment strategies for enhancing sewage sludge disintegration and subsequent anaerobic digestion: Current advances, full-scale application and future perspectives. Renew. Sust. Energ. Rev. 69, 559-577.

[48]Zinder, S.H., Anguish, T., 1992. Carbon monoxide, hydrogen, and formate metabolism during methanogenesis from acetate by thermophilic cultures of Methanosarcina and Methanothrix strains. Appl. Environ. Mirobiol. 58 (10), 3323-3329.

Table and figure captions

Table 1 Properties of the PDWW used in batch tests.

Table 2 Tests designed to verify the effect of ZVI addition on hydrolysis-acidification process.

Table 3 Influence of ZVI addition (6 g/L) on acetoclastic methanogenesis process by simulating Gompertz equation.

Fig. 1. The effect of F/M ratio on PDWW during AD: (a) variation of accumulative methane production and (b) BMP at different F/M ratios.

Fig. 2. The effect of ZVI dosage on PDWW during AD at F/M of 0.5: ((a) variation of accumulative methane production and (b) BMP at different ZVI dosages.

Fig. 3. The effect of ZVI on hydrolysis-acidification process: (a) variation of SCOD without BES addition and (b) variation of SCOD with BES addition.

Fig. 4. Organic acids accumulation with BES addition: (a) negative control; (b) positive control and (c) 6 g/L ZVI addition.

Fig. 5. The effect of ZVI on methanogenesis process with various substrates: (a) acetic acid; (b) propionic acid; (c) acetic acid and propionic acid mixture (5: 1) and (d) H_2 and CO_2 mixture (8: 2).

Table 1 Properties of the PDWW used in batch tests.

Batch tests	COD (mg/L)	SCOD (mg/L)	SCOD/COD (%)	TS (g/L)	VS (g/L)	VS/TS (%)	Polysaccharide (mg/L)	Protein (mg/L)
F/M ratio	2483±155	228.7±21.5	9.2	2.15±0.05	1.66±0.05	77.2	-	-
ZVI dosage	2528±147	439.6±32.7	17.4	1.55±0.02	1.13±0.01	72.9	-	-
Hydrolysis - acidification	1207.5±82.5	137.1±11.6	11.4	1.45±0.04	1.05±0.03	72.4	8.48±4.74	52.72±10.95

Table 2 Tests designed to verify the effect of ZVI addition on hydrolysis-acidification process.

Tested group	Seed sludge (mL)	Substrate (mL)	BES (mmol/L)	ZVI (g/L)
Negative control without BES	60	-	-	-
Positive control without BES	60	90	-	-
6 g/L ZVI addition without BES	60	90	-	6
Negative control with BES	60	-	50	-
Positive control with BES	60	90	50	-
6 g/L ZVI addition with BES	60	90	50	6

Table 3 Influence of ZVI addition (6 g/L) on acetoclastic methanogenesis process by simulating Gompertz equation.

Substrate	Sample	P_0 (LCH_4/gCOD)	R_{max} (L CH_4/gCOD)	t_0 (d)
Acetic acid	Positive control	0.336	0.241	0.8
	ZVI addition	0.337	0.255	1.0
Propionic acid	Positive control	0.344	0.098	1.2
	ZVI addition	0.331	0.091	1.3
Acetic acid and propionic acid	Positive control	0.338	0.240	0.7
	ZVI addition	0.319	0.199	0.9

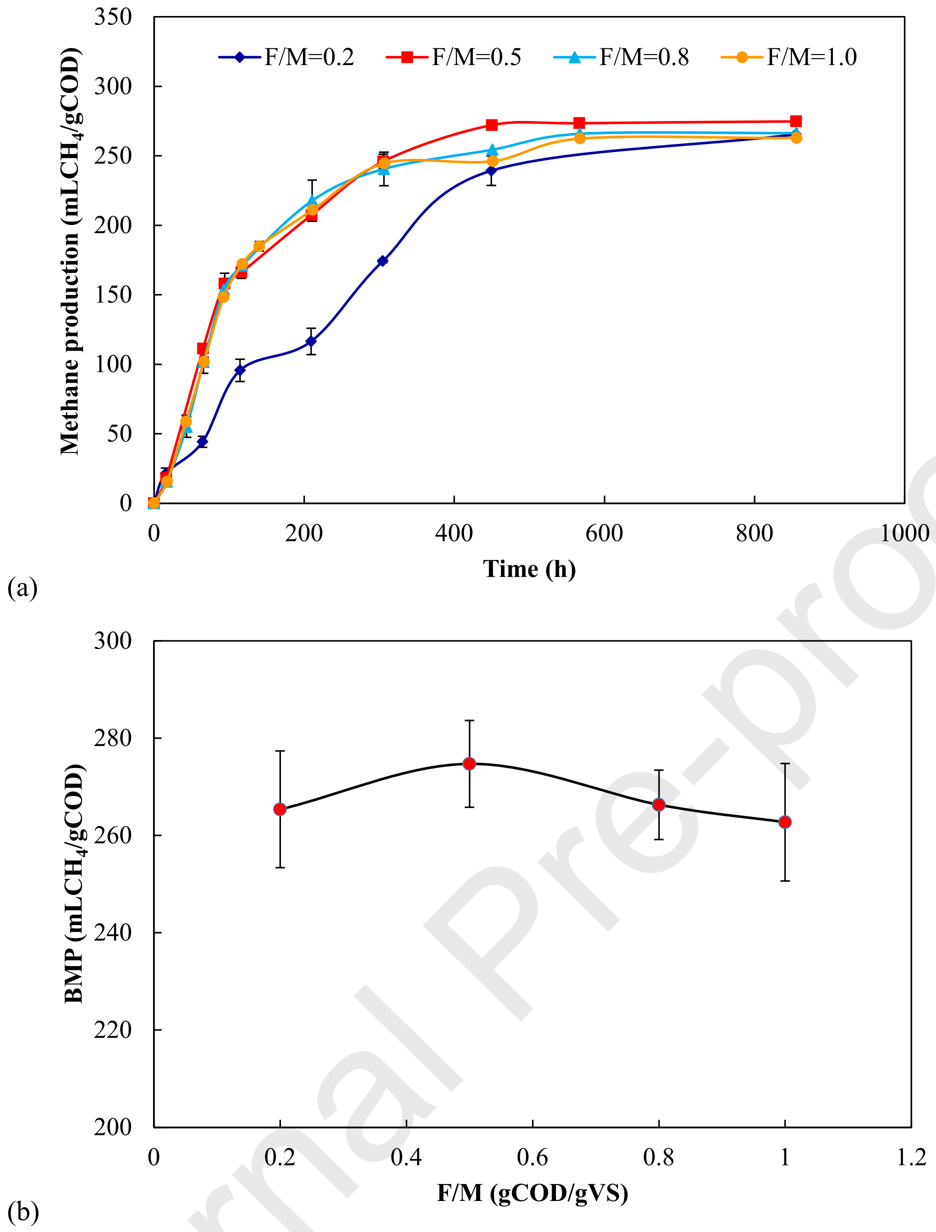
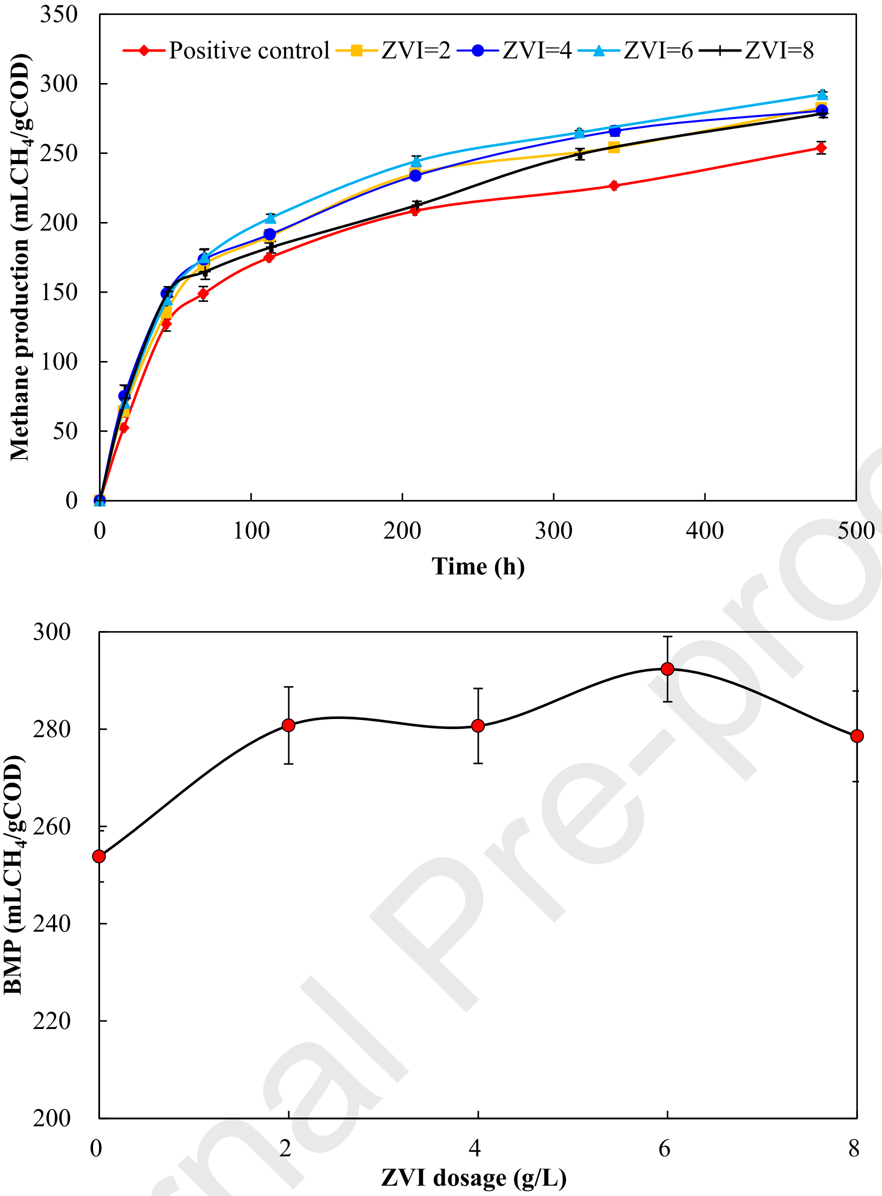

350
300
250
200
150
100
50
0
Methane production (mLCH$_4$/gCOD)
F/M=0.2
F/M=0.5
F/M=0.8
F/M=1.0
0
200
400
600
800
1000
Time (h)
(a)
300
280
260
240
220
200
BMP (mLCH$_4$/gCOD)
0
0.2
0.4
0.6
0.8
1
1.2
F/M (gCOD/gVS)
(b)

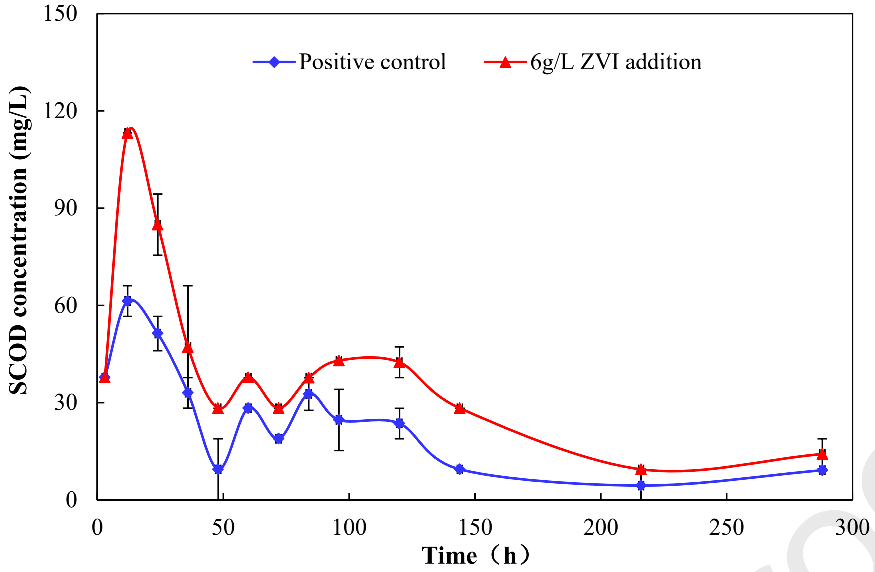
Fig. 1.


Positive control
ZVI=2
ZVI=4
ZVI=6
ZVI=8
Methane production (mLCH$_4$/gCOD)
0
50
100
150
200
250
300
350
0
100
200
300
400
500
Time (h)
BMP (mLCH$_4$/gCOD)
200
220
240
260
280
300
0
2
4
6
8
ZVI dosage (g/L)

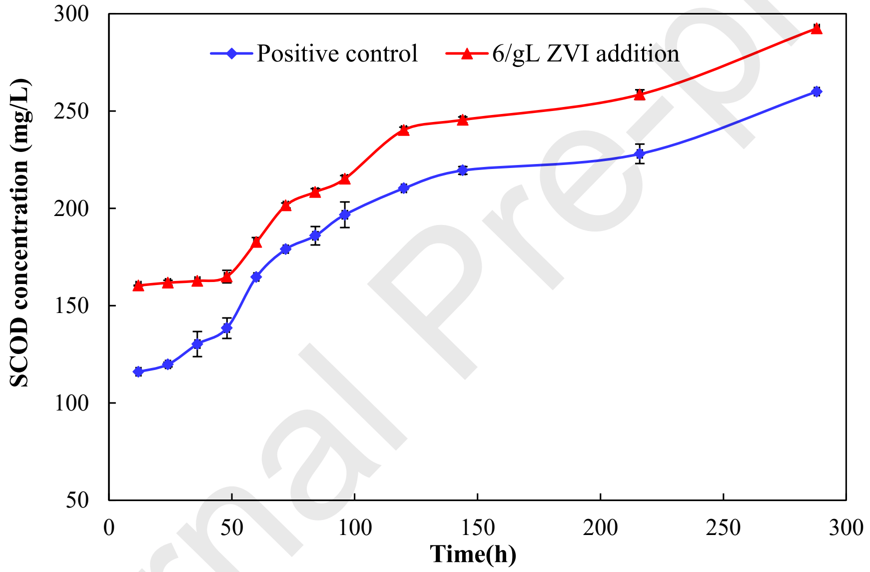
(a)

(b)

Fig. 2.


SCOD concentration (mg/L)
Time（h）
Positive control
6g/L ZVI addition
0
30
60
90
120
150
0
50
100
150
200
250
300

(a)


SCOD concentration (mg/L)
Time(h)
Positive control
6/gL ZVI addition
50
100
150
200
250
300
0
50
100
150
200
250
300

(b)

Fig. 3.

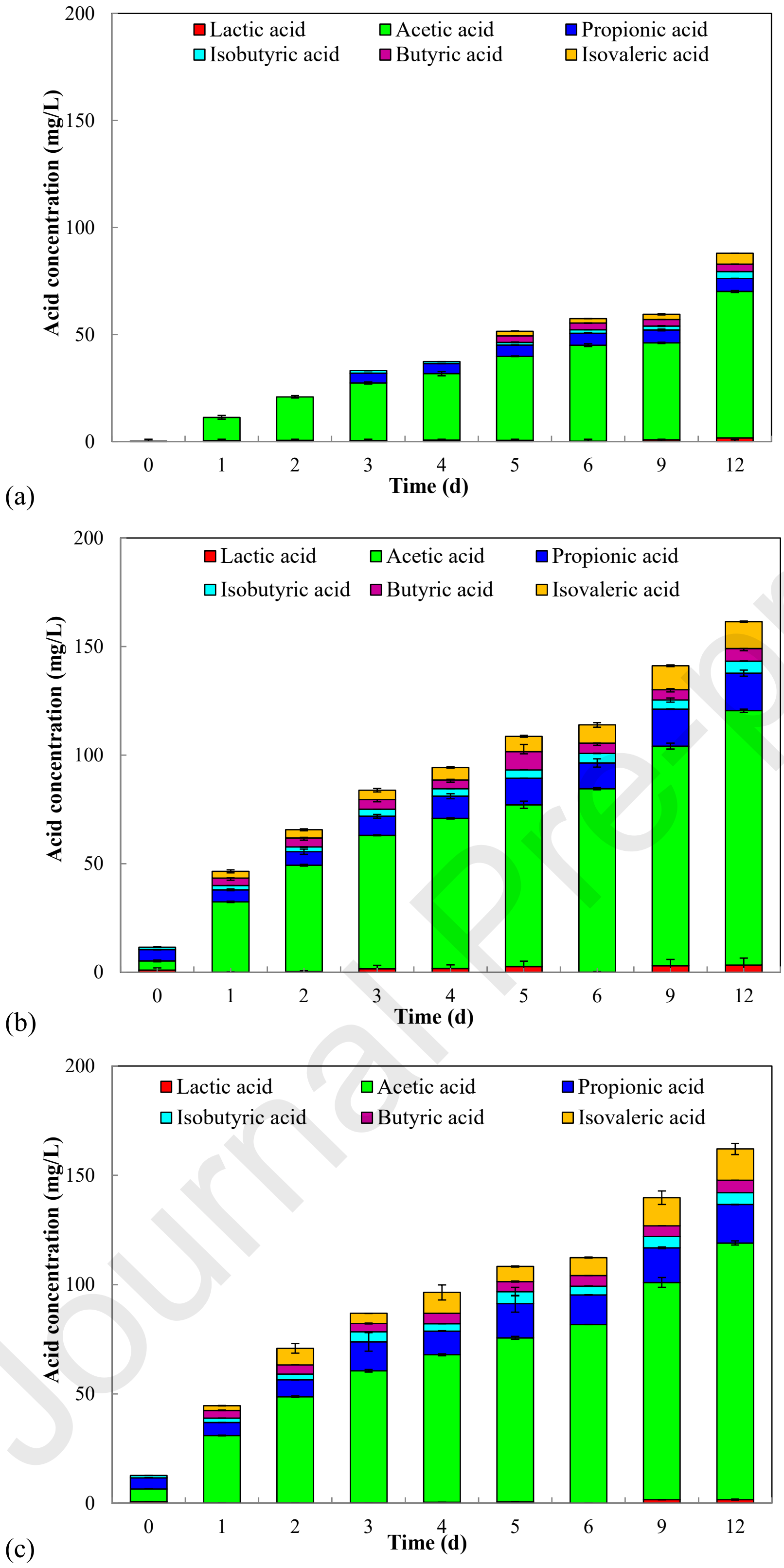
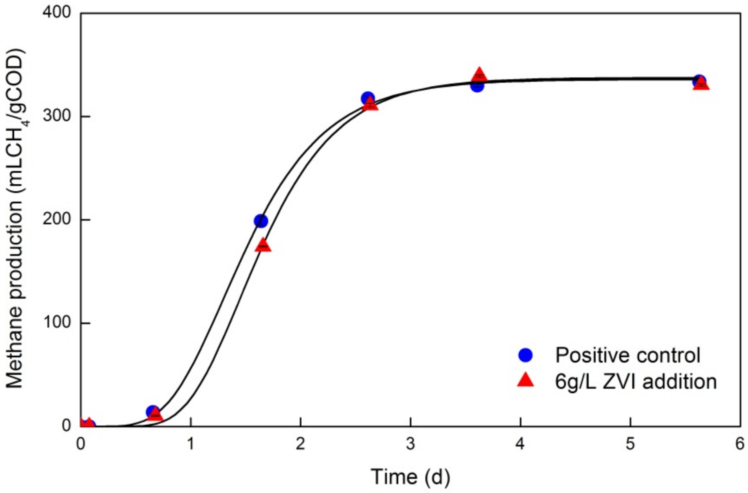
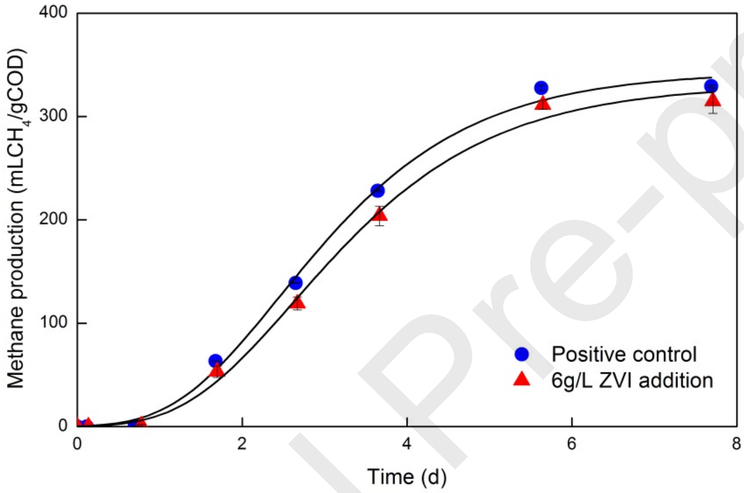

200
150
100
50
0
Acid concentration (mg/L)
Lactic acid
Acetic acid
Propionic acid
Isobutyric acid
Butyric acid
Isovaleric acid
0
1
2
3
4
5
6
9
12
Time (d)
(a)
(b)
(c)

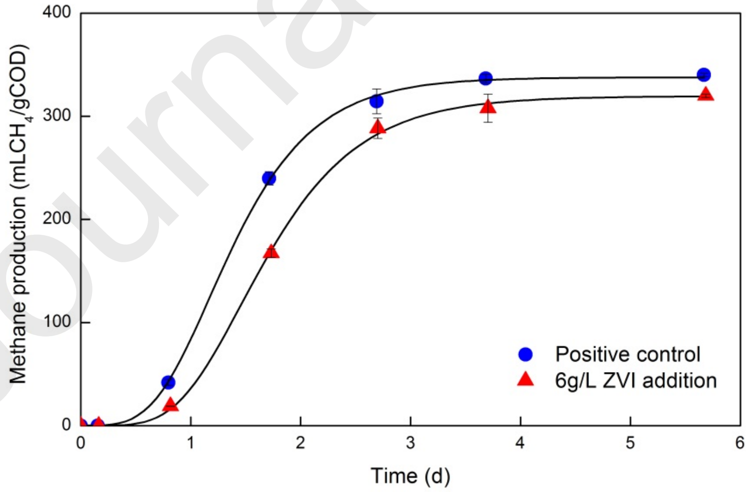
Fig. 4.


400
300
200
100
0
Methane production (mLCH$_4$/gCOD)
0
1
2
3
4
5
6
Time (d)
Positive control
6g/L ZVI addition

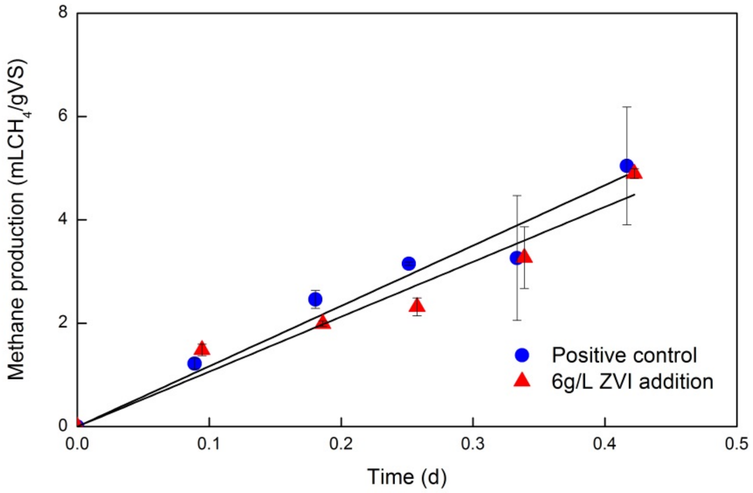
(a)


400
300
200
100
0
Methane production (mLCH$_4$/gCOD)
0
2
4
6
8
Time (d)
Positive control
6g/L ZVI addition

(b)


400
300
200
100
0
Methane production (mLCH$_4$/gCOD)
0
1
2
3
4
5
6
Time (d)
Positive control
6g/L ZVI addition

(c)



(d)

Fig. 5.

CRediT author statement

Zang Ying: Data curation, Investigation, Writing- Original draft preparation. **Yang Yuan**: Data curation, Investigation. **Hu Yisong**: Conceptualization, Supervision, Writing - Review and Editing. **Ngo Huu Hao**: Writing - Review and Editing. **Wang Xiaochang C.**: Project administration, Funding acquisition. **Li Yu-You**: Writing - Review and Editing.

Highlights

- Pre-concentrated domestic wastewater was assessed by batch BMP assay
- 6 g/L ZVI dosage at fixed F/M of 0.5 enhanced the BMP by 15.2%
- ZVI has improved hydrolysis process and regulated acidification process
- Pre-concentration plus AD is promising for wastewater resource recovery