Improved Algal Sludge Methane Production and Dewaterability by Zerovalent Iron-Assisted Fermentation

Shixiong Geng, Kang Song, Lu Li, and Fazhi Xie

ABSTRACT: This study investigated the methane production improvement of algal sludge by zerovalent iron (ZVI)-assisted anaerobic digestion. The zerovalent iron added were 0.5, 2, 5, 10, and 20 g ZVI/g TS (total solid). The results indicated that the addition of ZVI at 2, 5, 10, and 20 g ZVI/g TS has improved the methane production 1.07, 1.24, 1.41, and 1.46 times as compared with no ZVI added. The dewaterability of treated algal sludge has improved 1.06, 1.08, 1.08, and 1.11 times as compared with no ZVI addition. The biochemical methane production test results fitted to both one-substrate and two-substrate models. The one-substrate model indicated that the hydrolysis rate has increased 8.21, 7.07, 9.39, 3.50, and 5.07 times as compared with R1 where no ZVI was added. The two-substrate model implied that the rapid hydrolysis rate values were 5.23, 4.5, 5.98, 2.23, and 3.23 times as compared with R1. The one-substrate model predicted that the value of methane production was in high correlation with the actual value (R^2 > 0.98). The addition of ZVI in algal sludge for methane production without an extra pretreatment process has improved the hydrolysis rate and methane production. This has the potential to be developed as an effective and economic technology in resource recovery from algal sludge.

1. INTRODUCTION

Algal sludge collected from the algal bloom lakes is an important environmental pollution problem where the treatment and resource recovery of this waste algal sludge has aroused wide concern.1–3 Anaerobic digestion is a promising process in using algae biomass for producing methane biogas; however, the methane production rate is relatively low due to the low biodegradability of algae.4,5 Pretreatment technologies such as mechanical, ultrasound, microwave, thermal, chemical, biological, and combined processes have been investigated in improving the methane production from algae anaerobic digestion.1,2,6 Bai et al. reported that using free nitrous acid (2.31 mg HNO2-N·L⁻¹) as a pretreatment process has improved the algae methane production yield by 161 to 250 L·CH4/kg·VS added.8 Wang et al. found that free ammonia at 60–530 mg NH3-N/L has significantly improved the algae solubilization and methane generation during anaerobic digestion.2,7 Keymer et al. demonstrated that a high-pressure thermal hydrolysis process has increased the algae yield by 81%.9 Marsolek et al. achieved an increase of biogas production from 0.28 to 0.39 L biogas per g volatile solids by thermal pretreatment at 90 °C.10 All those pretreatment processes were used to improve the biodegradability or hydrolysis rate of the algae by disrupting the algae cell wall.

Zhen et al. reported that zerovalent scrap iron (ZVSI) stimulated the anaerobic digestion of sludge with the methane yield increased by 38.3% where the ZVSI has enhanced the methanogenesis as electron donors and accelerated the hydrolysis–acidification and methanation steps of the wasted activated sludge (WAS).11 It is also reported that the addition of zerovalent iron (ZVI) could accelerate the anaerobic digestion of sludge. Feng et al. achieved a methane production increase of 43.5% by using ZVI where the degradation of protein and cellulose was enhanced.12 Yang et al. investigated the nano ZVI on methanogenic activity during the anaerobic digestion, and the results indicated that ZVI at 30 mM increased methane production, while nano ZVI inhibited the methanogenic growth and methane production at concentration of 1 mM and above.13 Suanon et al. reported that the nanoscale ZVI and iron powder addition in sludge anaerobic digestion has enhanced the methane yield up to 25 and 40%, respectively.14 Zhang et al. indicated that the ZVI could enhance the methanogenic activity in the anaerobic sludge digestion.15 The total solid (TS) and total chemical oxygen

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demand (TCOD) of blue algae harvested from the algal bloom lakes have quite similar values as compared with the activated sludge that was used for anaerobic digestion. Microalgae contains a high portion of organic components including ash (5–17%), carbohydrate (18–46%), crude protein (18–46%), crude lipid (12–48%), and energy (19–27 MJ/kg). This implied that the ZVI, which was effectively applied in enhancing the methane production from WAS anaerobic digestion, could also be effective in the algal sludge methane production.

This study innovatively investigated the potential of methane production improvement for algal sludge anaerobic digestion by the assistance of ZVI. Biochemical methane production tests were used for accumulated methane production analysis for the ZVI-assisted algae fermentation under different ZVI dosages. The methane production potential and hydrolysis rate of ZVI-assisted algal sludge digestion were analyzed by one-substrate and two-substrate mathematical models. Economic analysis was conducted to assess the economic potential of the proposed algal anaerobic digestion process.

2. MATERIALS AND METHODS

2.1. Algal Sludge and Inoculum Sludge. The algal sludge used in this study was *Microcystis* sp. It was harvested from Guanqiao Base of Institute of Hydrobiology, Chinese Academy of Sciences, Wuhan, China. Over 98% of the algal sludge was *Microcystis* by the microscopic examination where the TS was 11.28 ± 0.24 g/L and the volatile solid (VS) was 9.23 ± 0.23 g/L. The inoculum sludge used was collected from the Sanjintan wastewater treatment plant (WWTP) anaerobic fermenter, Wuhan, China. A mesopholic anaerobic digestion process is used in the Sanjintan WWTP for wasted sludge digestion. The characteristics of inoculum sludge, such as TS, VS, TCOD, soluble chemical oxygen demand (SCOD), and pH, were shown in Table 1.

Table 1. Characteristics of the Algal Sludge and Seed Sludge Used in this Study

| parameters          | algal sludge       | seed sludge       |
|---------------------|--------------------|-------------------|
| TS (g/L)            | 11.28 ± 0.24       | 32.05 ± 1.01      |
| VS (g/L)            | 9.23 ± 0.23        | 12.71 ± 0.01      |
| TCOD (g/L)          | 11.28 ± 0.64       | 15.3 ± 0.19       |
| SCOD (mg/L)         | 323.58 ± 48.58     | 400.25 ± 32.75    |
| pH                  | 7.19 ± 0.01        | 6.36 ± 0.02       |

2.2. Zerovalent Iron Addition. The algal sludge was added with ZVI at concentrations of 0, 0.5, 2, 5, 10, and 20 g·ZVI/g·TS of the algal sludge before anaerobic digestion. The ZVI powder applied is of analytical grade with purity of 98%.

2.3. Biochemical Methane Potential Test. BMP tests were conducted to assay ZVI-assisted algal sludge anaerobic digestion methane production. The algae and inoculum were transferred to corresponding reactors at an initial VS ratio of 1:2. The reactor total volume is 310 mL in which 105 mL of inoculum and 70 mL of algal sludge were added. The ZVI powder, seed sludge, and algae were totally mixed and flushed with pure N2 gas for 5 min where anaerobic conditions were created. A blank test was also conducted where the seed sludge (105 mL) and MilliQ water (70 mL) instead of the algae were added in the reactor. The BMP test was thus started with the reactors sealed by a rubber stopper and shaken at a 37 ± 1 °C constant-temperature incubator. The batch tests were conducted in triplicate in each of the incubators for 57 days until the pressure increase in the reactors dropped to a negligible level. The pressure in each reactor was measured, and the biogas production from the reactors was collected every 2–4 days. The net biogas generation from the algae in each reactor was determined by subtracting the biogas produced by the blank reactor from each reactor. The methane production was calculated based on the multiplication of net biogas pressure increment in the reactor and the methane concentration produced. The methane production was recorded as the volume of methane produced per kg of the TS of the total algae and inoculum added in the reactor (L·CH4/kg·TS). The cumulative methane production was the summation of methane produced per day in the corresponding reactor. The BMP test experimental conditions were shown in Table 2.

Table 2. Experimental Design with Different ZVI Dosages

| reactor function | experimental conditions |
|------------------|-------------------------|
| R0 blank         | 105 mL of seed sludge + 70 mL of MilliQ water |
| R1 ZVI-0         | 105 mL of seed sludge + 70 mL of algal sludge |
| R2 ZVI-0.5       | 105 mL of seed sludge + 70 mL of algal sludge + 0.5 g·ZVI/g·TS |
| R3 ZVI-2         | 105 mL of seed sludge + 70 mL of algal sludge + 2 g·ZVI/g·TS |
| R4 ZVI-5         | 105 mL of seed sludge + 70 mL of algal sludge + 5 g·ZVI/g·TS |
| R5 ZVI-10        | 105 mL of seed sludge + 70 mL of algal sludge + 10 g·ZVI/g·TS |
| R6 ZVI-20        | 105 mL of seed sludge + 70 mL of algal sludge + 20 g·ZVI/g·TS |

2.4. Mathematical Modeling Analysis of BMP Test Results. The hydrolysis rate (k) and biochemical methane potential (B0) are two key parameters associated with the methane generation. Two models including one-substrate model and two-substrate model were used to simulate the BMP test results. The models were as shown in eqs 1 and 2.

\[
B(t) = B_0 \times (1 - e^{-k_{rapid}t}) + B_{0,slow} \times (1 - e^{-k_{slow}t})
\]

As shown in eqs 1 and 2, the \( B(t) \) is the cumulative methane production at day \( t \) (L·CH4/kg·TS, \( t = \text{time (day)} \)). \( Y \) (L·CH4/kg·TS) is the cumulative methane production in day \( t \) by the corresponding simulated equations 1 and 2. In the one-substrate model, \( B_0 \) is the biochemical methane potential (L·CH4/kg·TS), and \( k \) is the hydrolysis rate (day^{-1}). In the two-substrate model, the algae were considered as consisted of rapidly biodegradable components and slowly biodegradable substrates. \( B_{0,rapid} \) is the rapidly biodegradable substrates' biochemical methane potential (L·CH4/kg·TS), \( k_{rapid} \) is the hydrolysis rate of the rapidly biodegradable substrates (day^{-1}), \( B_{0,slow} \) is the biochemical methane potential of the slowly biodegradable substrates, and \( k_{slow} \) is the slowly biodegradable substrates' hydrolysis rate (day^{-1}). The two-substrate model is able to give information of rapidly and slowly biodegradable components of the ZVI-assisted algal sludge anaerobic
digested. The changes in the parameters \( B_{p0}, k, B_{p\text{rapid}}, B_{p\text{slow}}, k_{\text{rapid}}, \) and \( k_{\text{slow}} \) under various ZVI concentrations in each reactor can thus be compared.

### 2.5. Basic Parameters Analysis

The basic parameters of the inoculum and algae were tested in triplicate following standard methods (APHA, 2016). The TCOD, SCOD, pH, NH\(_4\)-N, and fluorescence excitation emission matrix (FEEM) of the algae and inoculum mixture were analyzed after the BMP test was stopped. FEEM was analyzed by a fluorescence spectrometer at emission wavelengths of 200–400 nm and excitation wavelengths at 280–540 nm (QM-4CW, PTI, USA). The dewaterability of the digested algal sludge was tested by measuring the free-water volume of sludge after being centrifuged at 3000 rpm for 30 min. The generated biogas pressure was measured by a manometer before sampling, and the actual volume was calculated from the pressure increase in the headspace volume (135 mL) and expressed at standard atmospheric pressure (25 °C, 1 atm). The methane concentration was measured by a GC analyzer (GC7890, Agilent, USA).

### 3. RESULTS AND DISCUSSION

#### 3.1. ZVI-Assisted Algal Sludge Methane Production Improvement

The cumulative methane production of the reactors with different ZVI concentrations added was shown in Figure 1. The accumulative methane production of algae kept increasing with time and approached a stable value at day 57. The final accumulative methane yield was 225.11, 227.36, 241.11, 279.69, 317.78, and 328.22 L CH\(_4\)/kg TS for ZVI addition at 0, 0.5, 2, 5, 10, and 20 g ZVI/g TS, respectively. The accumulative methane yield has enhanced 1.01, 1.07, 1.24, 1.41, and 1.46 times with the addition of ZVI at 0.5, 2, 5, 10, and 20 g ZVI/g TS as compared with no ZVI added, respectively. The algal sludge methane yield was rarely increased with ZVI concentration at 0.5 g ZVI/g TS while kept increasing with the ZVI dosage increased and achieved the highest value at a ZVI dosage of 20 g ZVI/g TS. The ZVI dosage and the accumulative methane production value were in linear correlation (Figure 2, \( R^2 = 0.8524 \)). This implied that the addition of ZVI has enhanced the accumulative methane production with ZVI dosage at 2 g ZVI/g TS and above. Zhen et al.\(^{11} \) reported that the ZVSI concentration at 1.0 g/g VSS has increased the WAS methane yield by 38.3% to a value of 174.9 mL/g VSS\(_{\text{feed}}\). The dosage used of ZVSI was a bit lower than the ZVI used in this study, which indicated that the algal sludge was more recalcitrant as compared with the WAS. The biogas generated in this study was much higher than the WAS as reported by earlier work, which indicated higher methane production potential of the algae.\(^{11}\) The ZVI added could have improved the algae solubilization during the fermentation process and thus improved biodegradability of the algae.\(^{1,8} \) The existence of ZVI powder also could provide physical effects in improving the algae cell disruption during the shaking process.\(^{14,18} \) The iron ions also could be reacted as an electron donor and change the pH in the reactor, thus causing the algae cell disintegration.\(^{11} \) Based on which, the algal sludge fermentation process was accelerated with the existence of ZVI, and the accumulated methane production was also improved.

#### 3.2. Biochemical Methane Potential Analysis

To understand the effect of ZVI addition in the enhancement of methane production for algal sludge, both one-substrate model and two-substrate model were used to simulate the methane production. Both one-substrate model and two-substrate model were fitted well with the methane production results in this study (Table 3, \( R^2 > 0.96 \) and Table 4, \( R^2 > 0.96 \)). The predicted biochemical methane production by the one-substrate model and the actual methane production value during the BMP test were in linear correlation (Figure 3, \( R^2 > 0.98 \)). As shown in Table 3, results of the one-substrate model shows that the hydrolysis rate \( k \) values of the algal sludge were 0.0028, 0.023, 0.0198, 0.0263, 0.0098, and 0.0142 day\(^{-1} \) for reactors with ZVI dosage at 0, 0.5, 2, 5, 10, and 20 g ZVI/g TS added. The hydrolysis rate of the reactors with ZVI added has improved 8.21, 7.07, 9.39, 3.50, and 5.07 times as compared with the control reactor where no ZVI was added. The \( k \) value is much lower than the earlier reported work of WAS, while the \( k \) value enhanced with the addition of ZVI was much higher.\(^{19-21} \) This implied that the ZVI has largely improved the hydrolysis rate of algae, not only promoted the algae cell disruption but also improved the hydrolyzed organic components’ biodegradability.\(^{11,18} \) This implied that with the existence of ZVI in the reactor, the hydrolysis rate of algae anaerobic digestion was improved. The predicted biochemical methane production by the one-substrate model was 247.50, 239.19, 257.42, 289.50, 338.19, and 344.48 L CH\(_4\)/kg TS in reactors R1 to R6, respectively. It is also shown in Table 3 that the pure algae without ZVI added has an extremely high \( B_{p0} \) and a low k value. This implied that the pure algae have a high methane potential but a low hydrolysis rate, which means that the methane production from pure algae might need a very long period and assistance methods are necessary.
The two-substrate model results show that the rapid hydrolysis rate $k_{\text{rapid}}$ values for R1 to R6 were 0.0044, 0.023, 0.0198, 0.0263, 0.098, and 0.0142 day$^{-1}$ (Table 4). The rapid hydrolysis rates for algal sludge with ZVI added at R2 to R6 were 5.23, 4.50, 5.98, 2.23, and 3.23 times as compared with the pure algae. The corresponding rapid biochemical methane potential $B_{\text{rapid}}$ values were 160.3, 189.21, 180.28, 395.25, and 308.72 for R2 to R6. All the reactors with ZVI added show higher rapid hydrolysis rates where higher ZVI dosage results in a higher $B_{\text{rapid}}$. The rapid hydrolysis rate for pure algae was quite low, and the $B_{\text{rapid}}$ was quite high. This was similar with the one-substrate model results. The slow hydrolysis rate $k_{\text{slow}}$ for pure algae was quite high with a value of 1914.85 day$^{-1}$, and the slow biochemical methane potential $B_{\text{slow}}$ has a negative value. This could summarize that the methane production rate for pure algae was much lower than that of the ZVI-assisted algae anaerobic digestion. The $k_{\text{slow}}$ for R2 to R6 were 0.023, 0.020, 0.026, 0.010, and 0.014 day$^{-1}$. The $B_{\text{slow}}$ for R2 to R6 were 167.16, 191.30, 192.46, 394.92, and 312.11 L CH$_4$/kg-TS. The $B_{\text{slow}}$ of reactors with higher ZVI added has a lower value as compared with R2 where ZVI was added at 0.5 g ZVI/g-TS. This summarized that both rapidly and slowly biodegradable components were improved with the assistance of ZVI addition.24,25

**Table 3. Determined Hydrolysis Rate ($k$) and Biochemical Methane Potential ($B_0$) of Algae at Different Reactors Using the One-Substrate Model**

| reactors | R1    | R2    | R3    | R4    | R5    | R6    |
|----------|-------|-------|-------|-------|-------|-------|
| $k$ (day$^{-1}$) | 0.0028 | 0.0230 | 0.0198 | 0.0263 | 0.0098 | 0.0142 |
| $B_0$ (L CH$_4$/kg-TS) | 1677.80 | 327.46 | 380.51 | 372.74 | 790.17 | 620.82 |
| $Y_{CH4}$ (L CH$_4$/kg-TS) | 247.50 | 239.19 | 257.42 | 289.50 | 338.19 | 344.48 |

**Table 4. Determined Hydrolysis Rate ($k$) and Biochemical Methane Potential ($B_0$) of Algae at Different Reactors Using the Two-Substrate Model**

| reactors | R1    | R2    | R3    | R4    | R5    | R6    |
|----------|-------|-------|-------|-------|-------|-------|
| $k_{\text{rapid}}$ (day$^{-1}$) | 0.0044 | 0.023 | 0.0198 | 0.0263 | 0.098 | 0.0142 |
| $B_{\text{rapid}}$ (L CH$_4$/kg-TS) | 1129.76 | 160.30 | 189.21 | 180.28 | 395.25 | 308.72 |
| $k_{\text{slow}}$ (day$^{-1}$) | 1914.85 | 0.023 | 0.0198 | 0.0263 | 0.098 | 0.0142 |
| $B_{\text{slow}}$ (L CH$_4$/kg-TS) | –3.6383 | 167.16 | 191.29 | 192.46 | 394.92 | 312.11 |
| $R^2$ | 0.9662 | 0.9853 | 0.9776 | 0.9882 | 0.9917 | 0.9904 |
| $Y_{CH4}$ (L CH$_4$/kg-TS) | 246.97 | 239.19 | 257.42 | 289.50 | 338.19 | 344.48 |

**Figure 3.** Actual and predicted biochemical methane potential by the one-substrate model ($R^2 > 0.98$).

**Figure 4.** TCOD and SCOD values of digested algal sludge.

3.3. Characteristics of the Digested Algal Sludge. The TCOD and SCOD of the digested algal sludge were shown in Figure 4. The SCOD/TCOD values of the digested algal sludge were 0.02, 0.03, 0.21, 0.35, 0.26, and 0.24 for ZVI added at 0, 0.5, 2, 5, 10, and 20 g ZVI/g-TS. The highest TCOD was shown in the pure algae reactor R1. The results indicated that the reactors with ZVI added above 0.5 g ZVI/g-TS has a much higher SCOD/TCOD even for the digested sludge. The ZVI added at 0.5 g ZVI/g-TS only slightly improved the SCOD/TCOD value, while the TCOD was also lower than the pure algae reactor. This implied that the ZVI addition has improved the biodegradability of the algal sludge and thus improved the methane production rate; this was in accordance with the BMP test results. It is also obvious that a high SCOD of around 3000 mg/L was retained in R3 to R6 for the digested sludge. The ZVI added has a lower value as compared with R2 where ZVI was added at 0.5 g ZVI/g-TS. This once again could conclude that ZVI addition has enhanced the SCOD release from the algae, improved the biodegradability of the algae, and results in improvement of methane production in the same period as compared with the pure algae.

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3.4. Dewaterability and Economics of the Treated Algal Sludge. The algal sludge has similar characteristics with wasted activated sludge and also shares the same problem of dewaterability, which finally affects the treatment costs. The dewaterability of the digested algal sludge was as shown in Figure 6. The reactors with ZVI added at 2 to 20 g ZVI/g TS have much higher dewaterability as compared with R1 and R2 where ZVI added were 0 and 0.5 g ZVI/g TS. This could conclude that the addition of ZVI also enhanced the dewaterability of the algal sludge. The ZVI could have promoted the algae cell disintegration and the release of free water, and this improved the digested algae biodegradability and dewaterability. The particle size of algal sludge also could be decreased with ZVI or iron ions as a conditioner and thus facilitated the filtration process and improved the dewaterability.27

The economic analysis of the ZVI-assisted algal sludge, ZVI +hydrogen peroxide, and conventional Fenton conditioning methods for sludge dewaterability improvement were conducted and compared by a desktop scaling-up study. In the economic analysis, the improvement in algal sludge dewaterability was assumed to be same for the three conditioning methods. As shown in Table 5, the ZVI-assisted process have much higher dewaterability as compared with R1 and R2 where ZVI added were 0 and 0.5 g ZVI/g TS. This could conclude that the addition of ZVI also enhanced the dewaterability of the algal sludge. The ZVI could have promoted the algae cell disintegration and the release of free water, and this improved the digested algae biodegradability and dewaterability. The particle size of algal sludge also could be decreased with ZVI or iron ions as a conditioner and thus facilitated the filtration process and improved the dewaterability.27

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Table 5. Economic Analysis of ZVI-Assisted Algal Sludge Dewaterability Enhancement

| parameters                   | ZVI conditioning (this study) | ZVI+H₂O₂ conditioning | classical Fenton conditioning (Fe(II)+H₂O₂) |
|-----------------------------|-------------------------------|------------------------|-------------------------------------------|
| dry sludge amount (ton/year)| 2340                          | 2340                   | 2340                                      |
| ZVI powder ($/year)         | 16,977                        | 16,977                 | 58,171                                    |
| ferrous chloride ($/year)   | 8488                          | 8488                   | 499                                       |
| H₂O₂ ($/year)               | 499                           | 499                    | 499                                       |
| total cost ($/year)         | 16,977                        | 25,964                 | 67,158                                    |
| total saving with only ZVI ($/year) | 50,181 = 67,158 - 16,977 (74.72%, $21.44/ton) | 27 |

Cited from Zhou et al. (2014).27

Figure 5. FEEM of digested algal sludge supernatants after 57 days of anaerobic digestion. (a) R1 - 0 ZVI, (b) R2 - 0.5 g ZVI/g TS, (c) R3 - 2 g ZVI/g TS, (d) R4 - 5 g ZVI/g TS, (e) R5 - 10 g ZVI/g TS, and (f) R6 - 20 g ZVI/g TS.

Figure 6. Dewaterability of the algal sludge after ZVI-assisted digestion stopped.

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savings in the industrial area. However, further investigation, especially for full-scale application, requires future verification of the results.

3.5. Perspectives of Algal Sludge Resource Recovery. The algal sludge collected from the algal bloom lakes has been an environmental problem for decades, and the algae biomass resource recovery is an important issue. This study indicated that adding ZVI at a dosage of 2 g-ZVI/g-TS and above could enhance the methane production from algal sludge, enhance the digested algal sludge dewaterability, and save cost. This study added ZVI directly into the fresh algae and started the anaerobic digestion without a complicated pretreatment process. This is also more convenient and energy-saving as compared with other studies, which used complicated pretreatment before the anaerobic digestion process. It is also reported that the ZVI was used for soil or groundwater remediation; thus, the environmental risk of reuse of the digestate with ZVI from this study could be ignored. This makes the ZVI-assisted algal sludge digestion more attractive for future industrial application. At the meantime, the ZVI recovery and reuse or ZVI-based materials to be integrated into an anaerobic digester should be further investigated.

4. CONCLUSIONS

This study investigated the methane production potential of algal sludge by the assistance of zerovalent iron addition. The results indicated that the addition of ZVI has improved the methane production and the dewaterability of the digested algal sludge. The addition of ZVI at 2, 5, 10, and 20 g-ZVI/g-TS has improved the methane production 1.07, 1.24, 1.41, and 1.46 times as compared with no ZVI addition. Both one-substrate model and two-substrate model fitted well with the biochemical methane potential test results. The addition of ZVI has enhanced the hydrolysis rate 3.5 to 9.39 times as model results of the one-substrate model and improved the rapid hydrolysis rate 2.23 to 5.98 times in the two-substrate model as compared with pure algae anaerobic digestion. The economic analysis results implied that the algal sludge dewatering has saved 74.72% of cost by using ZVI as compared with the conventional process in activated sludge treatment. The ZVI addition has the potential to be developed as an effective and economically friendly technology for algae resource recovery.

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Notes
The authors declare no competing financial interest.

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REFERENCES

(1) Cheng, J.; Yue, L.; Ding, L.; Li, Y.-Y.; Ye, Q.; Zhou, J.; Cen, K.; Lin, R. Improving fermentative hydrogen and methane production from an algal bloom through hydrothermal/steam acid pretreatment. Int. J. Hydrogen Energy 2019, 44, 5812–5820.
(2) Tabassum, M. R.; Xia, A.; Murphy, J. D. Comparison of pretreatments to reduce salinity and enhance biomethane yields of Laminaria digita harvested in different seasons. Energy 2017, 140, 546–551.
(3) Zhong, W.; Chi, L.; Luo, Y.; Zhang, Z.; Zhang, Z.; Wu, W. M. Enhanced methane production from Taihu Lake blue algae by anaerobic co-digestion with corn straw in continuous feed digesters. Bioresour. Technol. 2013, 134, 264–270.
(4) Uggetti, E.; Passos, P.; Solé, M.; García, J.; Ferrer, I. Biogas from algae via anaerobic digestion. Algal Biotechnology; Springer: 2016; pp 195–216. DOI: 10.1007/978-3-319-12334-9_11.
(5) Wang, Q.; Sun, J.; Liu, S.; Gao, L.; Zhou, X.; Wang, D.; Nghiem, L. D. Free ammonia pretreatment improves anaerobic methane generation from algae. Water Res. 2019, 162, 269–275.
(6) Rodriguez, C.; Alaswad, A.; Mooney, J.; Prescott, T.; Olabi, A. G. Pre-treatment techniques used for anaerobic digestion of algae. Fuel Process. Technol. 2015, 138, 765–779.
(7) Ward, A. J.; Lewis, D. M.; Green, F. B. Anaerobic digestion of algae biomass: a review. Algal Res. 2014, 5, 204–214.
(8) Bai, X.; Lant, P. A.; Jensen, P. D.; Astals, S.; Pratt, S. Enhanced methane production from algal digestion using free nitrous acid pre-treatment. Renewable Energy 2016, 88, 383–390.
(9) Keymer, P.; Ruffell, I.; Pratt, S.; Lant, P. High pressure thermal hydrolysis as pre-treatment to increase the methane yield during anaerobic digestion of microalgae. Bioresour. Technol. 2013, 131, 128–133.
(10) Marsolek, M. D.; Kendall, E.; Thompson, P. L.; Shuman, T. R. Thermal pretreatment of algae for anaerobic digestion. Bioresour. Technol. 2014, 151, 373–377.
(11) Zhen, G.; Lu, X.; Li, Y. Y.; Liu, Y.; Zhao, Y. Influence of zero valent scrap iron (ZVSI) supply on methane production from waste activated sludge. Chem. Eng. J. 2015, 263, 461–470.
(12) Feng, Y.; Zhang, Y.; Quan, X.; Chen, S. Enhanced anaerobic digestion of waste activated sludge digestion by the addition of zero valent iron. Water Res. 2014, 52, 242–250.
(13) Yang, Y.; Guo, J.; Hu, Z. Impact of nano zero valent iron (NZVI) on methanogenic activity and population dynamics in anaerobic digestion. Water Res. 2013, 47, 6790–6800.
(14) Suanon, F.; Sun, Q.; Li, M.; Cai, X.; Zhang, Y.; Yan, Y.; Yu, C. P. Application of nanoscale zero valent iron and iron powder during sludge anaerobic digestion: Impact on methane yield and pharmaceutical and personal care products degradation. J. Hazard. Mater. 2017, 321, 47–53.
(15) Zhang, Y.; Feng, Y.; Quan, X. Zero-valent iron enhanced methanogenic activity in anaerobic digestion of waste activated sludge after heat and alkali pretreatment. Waste Manage. 2015, 38, 297–302.

https://pubs.acs.org/10.1021/acsomega.0c00174
ACS Omega 2020, 5, 6146–6152
(16) Tibbetts, S. M.; Milley, J. E.; Lall, S. P. Chemical composition and nutritional properties of freshwater and marine microalgal biomass cultured in photobioreactors. J. Appl. Phycol. 2015, 27, 1109–1119.

(17) Carpenter, A. W.; Laughton, S. N.; Wiesner, M. R. Enhanced biogas production from nanoscale zero valent iron-amended anaerobic bioreactors. Environ. Eng. Sci. 2015, 32, 647–655.

(18) Liu, Y.; Zhang, Y.; Ni, B. J. Zero valent iron simultaneously enhances methane production and sulfate reduction in anaerobic granular sludge reactors. Water Res. 2015, 75, 292–300.

(19) Wang, Q.; Jiang, G.; Ye, L.; Yuan, Z. Enhancing methane production from waste activated sludge using combined free nitrous acid and heat pre-treatment. Water Res. 2014, 63, 71–80.

(20) Wang, Q.; Sun, J.; Zhang, C.; Xie, G. J.; Zhou, X.; Qian, J.; et al. Polyhydroxyalkanoates in waste activated sludge enhances anaerobic methane production through improving biochemical methane potential instead of hydrolysis rate. Sci. Rep. 2016, 6, 19713.

(21) Li, L.; Li, Z.; Song, K.; Gu, Y.; Gao, X. Improving methane production from algal sludge based anaerobic digestion by co-pretreatment with ultrasound and zero-valent iron. J. Cleaner Prod. 2020, 120214.

(22) Puyol, D.; Flores-Alsina, X.; Segura, Y.; Molina, R.; Padrino, B.; Fierro, J. L. G.; Martinez, F. Exploring the effects of ZVI addition on resource recovery in the anaerobic digestion process. Chem. Eng. J. 2018, 335, 703–711.

(23) Zhao, Z.; Zang, Y.; Li, Y.; Quan, X.; Zhao, Z. Comparing the mechanisms of ZVI and Fe3O4 for promoting waste-activated sludge digestion. Water Res. 2018, 144, 126–133.

(24) Pérez-Elvira, S. I.; Sapkait, I.; Fdz-Polanco, F. Separate digestion of liquid and solid fractions of thermally pretreated secondary sludge. Assessment and global evaluation. Braz. J. Chem. Eng. 2016, 33, 699–704.

(25) Yeneneh, A. M.; Sen, T. K.; Ang, H. M.; Kayaalp, A. Optimisation of microwave, ultrasonic and combined microwave-ultrasonic pretreatment conditions for enhanced anaerobic digestion. Water, Air, Soil Pollut. 2017, 228, 11.

(26) Zhen, G.; Lu, X.; Niu, J.; Su, L.; Chai, X.; Zhao, Y.; Niu, D. Inhibitory effects of a shock load of Fe (II)-mediated persulfate oxidation on waste activated sludge anaerobic digestion. Chem. Eng. J. 2013, 233, 274–281.

(27) Zhou, X.; Wang, Q.; Jiang, G.; Zhang, X.; Yuan, Z. Improving dewaterability of waste activated sludge by combined conditioning with zero-valent iron and hydrogen peroxide. Bioresour. Technol. 2014, 174, 103–107.

(28) Liu, X.; Xu, Q.; Wang, D.; Zhao, J.; Wu, Y.; Liu, Y.; Yang, Q. Improved methane production from waste activated sludge by combining free ammonia with heat pretreatment: Performance, mechanisms and applications. Bioresour. Technol. 2018, 268, 230–236.

(29) Rafique, R.; Poulsen, T. G.; Nizami, A.-S.; Asam, Z.-U.-Z.; Murphy, J. D.; Kielty, G. Effect of thermal, chemical and thermo-chemical pre-treatments to enhance methane production. Energy 2010, 35, 4556–4561.

(30) Zhao, X.; Liu, W.; Cai, Z.; Han, B.; Qian, T.; Zhao, D. An overview of preparation and applications of stabilized zero-valent iron nanoparticles for soil and groundwater remediation. Water Res. 2016, 100, 245–266.

(31) Singh, R.; Misra, V.; Singh, R. P. Synthesis, characterization and role of zero-valent iron nanoparticle in removal of hexavalent chromium from chromium-spiked soil. J. Nanopart. Res. 2011, 13, 4063–4073.