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Toward bioenergy recovery from waste activated sludge: Improving bio-hydrogen production and sludge reduction by pretreatment coupled with anaerobic digestion-microbial electrolysis cells

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Abstract

In this study, a novel technology named pretreatment coupled with anaerobic digestion-microbial electrolysis cells (AD-MECs) for waste activated sludge (WAS) reduction and renewable bioenergy recovery has been investigated. Results showed that, compared with the control pretreatment, the three pretreatment methods used had greatly enhanced the performance of AD-MECs process, and efficient sludge reduction was achieved, especially in heat-alkaline pretreatment, 36.9% and 46.7% for total suspended solid (TSS) and volatile suspended solid (VSS) removal in 6 days. MECs fed with fermented WAS, displayed positive potential for bioenergy recovery, and the highest bio-hydrogen yield was 20.30 mg H_2/g VSS. Kinetic models indicated that with initial concentrations of soluble organic matters increasing, the bio-hydrogen yields of MECs increased linearly ($R^2 = 0.8903 \sim 0.9742$). The results above suggested that the novel technology proposed in this work showed attractive potential for renewable bioenergy recovery and sludge reduction.

Keywords: Anaerobic digestion, Microbial electrolysis cells, Waste activated sludge, Sludge reduction, Bioenergy recovery.

1. Introduction

The industrialisation and current population growth have led to rapidly increasing energy consumption.[1] In 2008, 88% of world energy demand was supplied by fossil fuels, such as oil (35%), coal (29%) and natural gas (24%).[2] However, the depletion of coal supply is predicted by 2112, and depletion of oil and gas reserves by 2042, thus, a rapid transition to renewable energy is needed in the near future.[3] Based on renewable energy production and emissions reduction of the greenhouse gas, energy dependency, associated with fossil fuels, has made anaerobic digestion (AD) of renewable biomass as an attractive option.[4, 5] Thus, biogas, especially bio-hydrogen, produced from renewable biomass by the potential mean of AD process has received intense attention.[6, 7]

Recently, waste activated sludge (WAS) as the operation by-product of wastewater treatment plants (WWTPs), its production has been increased significantly with the rapid development of population and urbanization.[8, 9] At present, although some approaches (landfill, incineration, land-use, etc.) could effectively solve the WAS problems, the effects followed are not friendly to both environment and ecosystem.[1, 10, 11] Meanwhile, costs of treatment methods mentioned above are very high, accounting for approximately 40-60% operation cost of WWTPs.[10] Thus, it is particularly important to develop effective and environmental techniques for WAS treatment.

The WAS can be used as a source of valuable chemical productions, but the main feature may be as promising feedstocks for renewable biofuels. [1] Currently, lots of researches have investigated the efficiencies of biogas and nutrients recoveries by AD process from WAS. [1, 7-15] However, it is well known that WAS hydrolysis is the rate-limiting step, resulting in low efficiency but high cost.[8-15] With the purpose to enhance the performance of AD process, a series of researches on WAS pretreatment have been done, aiming to improve WAS hydrolysis, such as biological, chemical, mechanical and co-digestion, etc. [9, 12, 16-18] In order to further improve WAS utilization, some previous studies have reported that it is possible to make the fermented liquid (mainly consisted of soluble protein, soluble carbohydrate, volatile fatty acids (VFAs), etc.) of WAS as the substrates for microbial electrolysis cells (MECs) to produce bio-hydrogen.[19, 20] However, one significant shortage of above researches is that the efficiency of sludge reduction has not been investigated. And another is that, though the positive effects of bioenergy recovery can be achieved, membrane filtration of fermented WAS is needed, while using the fermented liquid as the substrate for MECs, which leads to complicate bio-hydrogen production line and increase operation cost. Therefore, it is essential and meaningful to look for innovation and improved process.

Based on the knowledge obtained from previous investigations, making fermented WAS as the substrate of MECs directly for bio-hydrogen production, on one hand, could enhance the buffering capacity of the AD process, improve bioenergy production, and increase the positive synergisms established in the digesters, on the other hand, would improve the utilization efficiency of existing digesters at WWTPs and reduce the collection and transport cost of other decentralized organic matter. [13, 21]

However, little information is available regarding the pretreatment coupled with AD-MECs for bioenergy recovery and sludge reduction.

This work proposes to investigate the performances of pretreatment coupled with AD-MECs for sludge reduction and bioenergy recovery, while WAS is used as the substrate. The outcome of this study will establish some fundamentals that permit on the further exploration of novel bioenergy recovery and sludge reduction technique for the potential improvement of AD process.

2. Materials and methods

2.1 WAS source and characteristics

WAS used in this study was taken from the secondary sedimentation tank of Taiping Municipal Wastewater Treatment Plant running with anaerobic-anoxic-aerobic (A^2/O) system, Harbin, China. The WAS firstly was thickened by gravitational sedimentation for 24 h at 4 ℃, then screened with a 1 mm sieve to remove impurities, finally stored at 4 ℃ prior for later use and test. The main characteristics of WAS were: total suspended solids (TSS) 15.23 g/L, volatile suspended solids (VSS) 8.03 g/L, total chemical oxygen demand (TCOD) 13582 mg/L, soluble chemical oxygen demand (SCOD) 267 mg/L, soluble protein 14 mg COD/L, soluble carbohydrate 13.53 mg COD/L, VFAs 210 mg COD/L and pH 6.92.

2.2 Potential technique for waste activated sludge treatment

In this study, in order to simplify the previously employed processes for WAS reduction,[19, 20] the fermented WAS obtained after 3-day anaerobic fermentation was directly added to MECs to produce hydrogen. The detailed technological process was shown in Fig.1. Firstly, three typical pretreatment methods (heat-alkaline, freeze-thaw and ultrasonication) were used to pretreat WAS respectively to enhance WAS hydrolysis. Secondly, each pretreated WAS was fermented by a continuous stirred tank reactor (CSTR) under anaerobic condition to enhance concentrations of soluble organic matters (mainly soluble protein, soluble carbohydrate, and VFAs, especially VFAs). Thirdly, fermented WAS was directly added into MECs to produce hydrogen. The whole process was named pretreatment coupled with AD-MECs process, which might be a positively potential technique for sludge reduction and renewable energy recovery from WAS.

2.2.1 Pretreatment methods

The detailed conditions for WAS pretreatment methods were: (1) The control was operated simultaneously with no pretreatment to WAS. (2) The heat-alkaline pretreatment was carried out by firstly adding NaOH with dosage 0.105 g/g VSS, then keeping 81 ℃ for 20 minutes. [23] (3) The freeze-thaw pretreatment was carried out by firstly freezing at -18 ℃ for 72 h, then thawing at ambient temperature, 22 ± 2 ℃.[24] (4) The ultrasonication pretreatment was carried out with power density 0.5 W/mL for 10 minutes.[25] All treatments above were carried out in triplicate.

2.2.2 Anaerobic digestion set-up and operations

The CSTR, whose maximum working volume was 2.0 L, was used as anaerobic fermentation reactor. And the working volume was 1.0 L in this work. The operation conditions were: temperature 35 ±2 ℃, stirring rate 110-120 r/min, sludge retention time (SRT) 72 h. [26] Nitrogen gas was introduced to the reactors for 15 min to remove oxygen, and all tests were also carried out in triplicate.

2.2.3 MECs set-up and operations

MECs used in this study were set up on the basis of previous study.[19] And the working volume was 40 mL, including a 28 mL chamber (3 cm diameter × 4 cm length) and a 10 mL injection syringe (total volume 12 mL). The detailed parameters of anode and cathode can be found in the previous publication.[20] In this work, there were 12 single chamber MECs. The MECs were inoculated by WAS mentioned in Section 2.1 and were fed with acetate in start-up stage.[28] The detailed information on start-up of MECs could be found in the research of Liu et al.[19]. After the start-up of MECs, every 3 MECs were operated in parallel, resulting in four groups, named control, heat-alkaline, freeze-thaw and ultrasonication pretreatments, respectively. Then fermented WAS was used as carbon source for hydrogen production in 72-h batch operations. All MECs were synchronously operated for three cycles. And the operation temperature were 22 ±2 ℃, ambient temperature.

2.3 Analytical methods

WAS samples were centrifuged at 10000 rpm for 10 minutes, then supernatant samples were filtered by 0.45 μm cellulose nitrate membrane filters and finally filtrated samples were stored at 4 ℃ prior to analysis, of which, the VFAs, soluble carbohydrate and protein were analyzed immediately. Measurement methods for TSS, VSS, SCOD, TCOD, VFAs, soluble carbohydrate, soluble protein and pH could be found in the previous publications.[17, 20] VFAs were recorded as the sum of acetic (HAc), propionic (HPr), n-butyric (n-HBu), iso-butyric (iso-HBu), n-valeric (n-HVa), and iso-valeric acids (iso-HVa). Soluble carbohydrate, soluble protein and VFAs concentrations were converted to chemical demand oxygen (COD) with unit of mgCOD/L. And details about COD conversion coefficients were the same as the previous publications. [20] Measurement methods of currents, and both volume and component of gas produced by MECs were consistent with the researches.[19, 20]

2.4 Calculation methods

Both energy and coulombic efficiencies were calculated to characterize the performance of MECs. Calculation methods of energy and coulombic efficiencies were consistent with the researches.[19, 20] Software SPSS 17.0 had been used to analyze experimental data.

The coulombic efficiency (CE) was calculated by the following equation:

$$CE = Q_C/Q_T \times 100\% \quad (1)$$

Where Q_C was current coulombs calculated by the equation $Q=I\times t$, C and Q_T was coulombs of acetate used, C.

Energy efficiency (η_E) was calculated by the following equations:

$$\eta_E = W_{H2}/W_E \times 100\% \quad (2)$$

$$W_{H2} = n \times \Delta H \quad (3)$$

$$W_E = Q \times E_{ap} \quad (4)$$

where W_{H2} was the combustion heat of hydrogen produced, kJ, W_E was the electricity input, kJ, n was the moles of hydrogen production under standard conditions, mol, ΔH was the combustion heat of 1mol hydrogen, 285.83 kJ/mole H_2, and E_{ap} was the external voltage, 0.8V.

The removal efficiencies of both TSS and VSS, and average reduction rate of both TSS and VSS were defined as the following equations:

$$TSS\ removal = (TSS_0 - TSS_t)/\ TSS_0 * 100\% \quad (5)$$

$$VSS\ removal = (VSS_0 - VSS_t)/\ VSS_0 * 100\% \quad (6)$$

$$V_{TSS} = (TSS_0 - TSS_t)/t \quad (7)$$

$$V_{VSS} = (VSS_0 - VSS_t)/t \quad (8)$$

Where TSS_0 and VSS_0 were the initial values, g/L, respectively, TSS_t and VSS_t were the end values, g/L, respectively, and t was the operating time of AD-MECs process, 6 days.

3. Results and discussion

3.1 Performance of anaerobic fermentation and MECs start-up

The characteristics of pretreated WAS after 3-day anaerobic fermentation were shown in Table 1. As shown in Table 1, compared with control, SCOD concentrations of other three pretreatments had been greatly enhanced, indicating these three pretreatment methods could improve the WAS hydrolysis efficiently. It was consistent with the previous studies.[22-27] Also it could be concluded that heat-alkaline pretreatment could perform better than both freeze-thaw and ultrasonication pretreatments, while SCOD concentration obtained in heat-alkaline pretreatment were 2.4 and 1.5 times more than freeze-thaw and ultrasonication pretreatment, respectively. The possible reason was that, compared with freeze-thaw and ultrasonication pretreatments, the release of intracellular and/or extracellular constituents from the cells and/or extracellular polymeric substances (EPSs) to suspension was more effective in heat-alkaline pretreatment, and then WAS hydrolysis/acidification was much improved.[14-17, 23] By analyzing the components of SCOD in Table 1, it was obvious that VFAs was the highest soluble component in the fermented WAS, 67.9% for control, 40.6% for heat-alkaline pretreatment, 56.1% for freeze-thaw pretreatment and 50.1% for ultrasonication pretreatment. As exhibits in Fig. 2(a), except for control pretreatment, the percentages of HAc were relatively higher than other five components of VFAs mentioned in Section 2.3, especially heat-alkaline and ultrasonication pretreatments, accounted for 44.4% and 45.9%, respectively. Wang et al. had reported that VFAs were easy to be utilized by MECs to produce hydrogen. [19, 20] Thus, compared with control, the pretreatment methods had positively enhanced efficiencies of anaerobic fermentation processes of WAS, and suggested the feasible potential using fermented WAS in MECs.

Liu et al. had reported that it could obtain positive effects, while acetate was used as the carbon source for MECs start-up.[28] The 12 MECs were performed as replicates using acetate for anodic biofilm enrichment. Fig. 2(b) depicts SCOD removal, coulombic efficiencies, energy efficiencies and hydrogen production rate of MECs at start-up stage. As shown in Fig.2(b), coulombic efficiencies of all MECs were stabilized at 108.3 ± 5.2%, the corresponding SCOD removal and energy efficiencies were 86.1 ±2.1% and 121.3 ±9.9% with current peak (4.12 ±0.33) mA, respectively. All MECs had similar abilities to convert acetate to hydrogen, 0.91 ±0.08 $m^3/(m^3 \cdot d)$ at 24-h retention time. Results above indicated that MECs had been started up successfully. [19] After MECs start-up, these 12 MECs were divided into four groups, three MECs of each group operated in parallel for hydrogen production by feeding with fermented WAS, named G1 (control pretreatment), G2 (heat-alkaline pretreatment), G3 (freeze-thaw pretreatment) and G4 (ultrasonication pretreatment), respectively.

3.2 Performance of AD-MECs on sludge reduction

Currently, biological methods, especially anaerobic fermentation, are given priority to achieve sludge reduction. [1, 10, 11] In this paper, effects of a novel technology, named pretreatment coupled with AD-MECs, had been investigated for sludge reduction (Fig.3). As shown in Fig. 3(a), compared with raw WAS, TSS and VSS of experiment pretreatments were all reduced significantly, especially heat-alkaline pretreatment, the corresponding removal efficiencies were 36.9% and 46.7%, respectively. Ordering the TSS and VSS reductions were heat-alkaline > ultrasonication > freeze-thaw > control pretreatments. This was consistent with results of anaerobic fermentation, indicating that WAS pretreatment had enhanced sludge reduction of AD-MECs process. The possible reason was that WAS hydrolysis/acidification greatly strengthened by pretreatment, then bio-hydrogen production and sludge reduction by AD-MECs process was positively enhanced.[1, 29, 30]

United States Environmental Protection Agency (USEPA) had reported that, when VSS removal efficiency was more than 38%, sludge reduction could be achieved. [31, 32] As shown in Fig. 3(b), both heat-alkaline and ultrasonication pretreatments coupled with AD-MECs for sludge reduction all met the USEPA standard, 46.7% and 43.9% for VSS removal, which were 2.56 and 2.40 times more than control pretreatment, respectively. Also, sludge reductions observed in heat-alkaline and ultrasonication pretreatments were higher than 38.7% for VSS reduction observed by Xiao et al. [33], who had used microbial fuel cells (MFCs) to achieve sludge reduction. So just taking sludge reduction into consideration, both processes above were better choices.

3.3 Bio-hydrogen production and energy recovery

In recent years, many researchers have reported biogas production from WAS by AD process. [1, 10-12, 15, 34-36] A potential technique, AD-MECs process, were used to enhance bio-hydrogen production by feeding pretreated WAS in this work. Fig.4 shows the bio-hydrogen production and energy efficiency. As shown in Fig. 4(a), in 72-h retention time, the highest bio-hydrogen production rate was obtained in heat-alkaline pretreatment, 0.67 $m^3 \cdot (m^3 \cdot d)^{-1}$, then followed by ultrasonication and freeze-thaw pretreatments. The possible reasons might be that, heat-alkaline pretreatment had enhanced WAS hydrolysis/acidification more effectively than the other two pretreatments, which provided the preferred substrate for MECs to produce bio-hydrogen[19], and the different initial pH of different fermented WAS (Table 1), might also influence the performance of MECs. [36-38] Ruizv et al. had reported the effects of pH on hydrogen production of MECs fed with acetate, and results showed that pH control was beneficial for the MEC performance.[37] By contrast, Kyazze et al. have reported that at an applied voltage of 850 mV, the difference in hydrogen production rates at pHs 5, 7 and 9 was however not statistically significant at the $P < 0.05$ level.[39] Moreover, the microbial communities in different pretreatments might be not consistent, which might further influence the performances of MECs. Sun et al. had reported difference of the microbial communities of MECs directly fed with alkaline-pretreated WAS and raw WAS, and pretreatment method had caused positive effects on microbial communities to produce hydrogen.[40] Compared with the experimental pretreatments, the control pretreatment had the lowest hydrogen production rate, this may be caused by the following two reasons, on one hand, soluble organic matters, especially VFAs of control pretreatment were the lowest, leading to poorest activities of hydrogenogens in MECs, on the other hand, during the operation process, the hydrogen produced would be consumed by other microorganisms in MECs because of substrate deficiency. [19, 41]

The highest hydrogen yield was also obtained in heat-alkaline pretreatment, 20.30 mg H_2/g VSS (Fig. 4a), which was 2.38 and 1.84 times more than that obtained in the previous researches reported by Liu et al. [19] and Wang et al. [20]. Meanwhile, the bio-hydrogen yield obtained in ultrasonication pretreatment was 1.82 and 1.40 times more than that obtained in the above studies, respectively[19, 20]. These attractive results might be attributed to the fact, compared with fermented liquid of WAS, microbial species contained in fermented WAS were much more abundant, some fermentative bacteria first utilized various sugars and amines to produce organic acids (e.g. acetate, propionate, and butyrate), which are subsequently metabolized by exoelectrogens for electricity generation. [41, 42] In the researches of both Lu et al. and Sun et al., [22, 40] fermented WAS after alkaline pretreatment was used as substrate of MECs to produce bio-hydrogen. The bio-hydrogen yields were 15.08 mg H_2/g VSS and 14.2 ±0.4 mg-H_2/g VSS, respectively, which were equivalent with ultrasonication pretreatment (15.48 mg H_2/g VSS) of this study, but lower than that in heat-alkaline pretreatment (20.30 mg H_2/g VSS). This phenomenon might be attributed to the followings reasons. On one hand, compared with alkaline pretreatment, more positive effects of heat-alkaline pretreatment and equivalent effects of ultrasonication pretreatment on WAS hydrolysis/acidification achieved. On the other hand, the changes of microbial communities in MECs, which were caused by fermented WAS after heat-alkaline or ultrasonication pretreatments, might be more beneficial than that of alkaline pretreatment. [43, 44] Therefore, heat-alkaline and ultrasonication pretreatments coupled with AD-MECs performed well for bio-hydrogen production from WAS.

As shown in Fig. 4(b), it was obvious that energy efficiencies of other three pretreatments were higher than 100%, 129.8%, 107.9% and 117.7% for heat-alkaline, freeze-thaw and ultrasonication pretreatments, respectively. Similar conclusions could be found in previous publications, [9, 20, 22] positive energy recovery could be realized, while using pretreated WAS as the substrate for MECs to produce bio-hydrogen. It suggested that three pretreatment methods used in this study coupled with AD-MECs for WAS treatment could achieve net energy recovery.

3.4 Kinetic models

In order to evaluate influences of initial concentrations of soluble protein, soluble carbonhydrate, and VFAs on bio-hydrogen yield of MECs, and the possible relationships between TSS and VSS reduction and bio-hydrogen yields, software SPSS17.0 was used to build mathematical statistical models. As shown in Fig. 5(a), bio-hydrogen yield increased linearly with initial concentrations of soluble organic matters increased, indicating that performance of AD stage was positive for enhancing bio-hydrogen production in the MECs process. Relationships between initial concentrations of soluble organic matters and bio-hydrogen yields can be expressed as Eq. (9) by linear regression analysis.

$$\begin{cases} Y_{\text{IVFAsC}} = 68.17X_{\text{hydrogen yield}} + 473.53,\ R^2 = 0.9742; \\ Y_{\text{ISPC}} = 64.75X_{\text{hydrogen yield}} + 27.14,\ R^2 = 0.9194; \\ Y_{\text{ISCC}} = 22.20X_{\text{hydrogen yield}} - 45.63,\ 27.14,\ R^2 = 0.8903. \end{cases} \quad (9)$$

Where Y_{IVFAsC}, Y_{ISPC} and Y_{ISCC} are initial VFAs, soluble protein, soluble carbonhydrate concentrations, respectively, mg/L. And $X_{\text{hydrogen yield}}$ is bio-hydrogen yield, mg H_2/g VSS.

According to the kinetic slopes from Eq. (9), it was obvious that initial concentrations of VFAs presented more significant effect on bio-hydrogen production, then followed by soluble protein and soluble carbonhydrate. This might be due to two reasons. Firstly, VFAs were the most suitable substrate for MECs to produce hydrogen in a WAS recycling system. [19, 20, 40, 42] Secondly, VFAs could be formed from protein and carbonhydrate. Chen et al. had reported that HAc, n-HBu and HPr were formed directly from the fermentation of protein and carbonhydrate, and the higher molecular weight SCFA such as n-HVa, were largely relevant to the fermentation of protein. [15, 45] Meanwhile, n-HBu, HPr and n-HVa were easily biodegraded to HAc in the anaerobic fermentation system. [45, 46] Thus, the kinetic models above indicated that the more concentrations of soluble organic matters in influent of MECs, the more bio-hydrogen produced.

Fig. 5(b) exhibits linear relationships between TSS and VSS removal efficiencies and bio-hydrogen yields. It can be observed that, VSS had higher removal efficiencies than that of TSS with same bio-hydrogen yields, meanwhile, TSS and VSS had higher removal efficiencies with higher bio-hydrogen yields. It was indicated that the organic matters of TSS and VSS were further converted to bio-hydrogen by the functional microorganisms in the MECs, resulting in an increased hydrogen production, as well as increased TSS and VSS removal efficiencies. Sun et al. had reported that the MECs fed with alkaline-pretreated WAS, had higher both hydrogen production and removal efficiencies of total solid (TS) and VSS than that fed with raw sludge.[40] The relationships between TSS and VSS removal efficiencies and bio-hydrogen yields can be expressed as Eq. (10) by linear regression analysis.

$$\begin{cases} Y_{\text{VSS removal}} = 1.44X_{\text{hydrogen yield}} + 19.68,\ R^2 = 0.9621; \\ Y_{\text{TSS removal}} = 1.12X_{\text{hydrogen yield}} + 14.11,\ R^2 = 0.9179. \end{cases} \qquad (10)$$

Where $Y_{\text{TSS removal}}$ and $Y_{\text{VSS removal}}$ are TSS and VSS removal efficiencies, respectively, %. And $X_{\text{hydrogen yield}}$ is hydrogen yield, mg H_2/g VSS.

3.5 Outlook of this work

A positively potential technique named pretreatment coupled with AD-MECs for renewable bio-hydrogen production and WAS reduction had been proposed in this work. Results showed that the process performed good efficiencies on both sludge reduction and bio-hydrogen production. The pretreatment methods were important to WAS utilization, however, few reports mentioned the subsequent effects to cascade utilization of WAS, which might be caused by initial treatment. Hereby, this study was designed to disclose the effects from WAS pretreatment to AD-MEC coupling system.

In our previous study, we had made the fermented liquid of WAS as the substrate of MECs for hydrogen production successfully, [19,20] and in the research of Sun et al., alkaline pretreated WAS was directly used as substrate for MECs to improve hydrogen recovery from WAS.[40] In the study of Lu et al., alkaline pretreated WAS after 8-day fermentation had been used as the substrate for MECs to produce hydrogen from WAS.[41] Based on the previous studies, we proposed the process, named pretreatment coupled with AD-MECs, might be possible to enhance the bio-hydrogen production from WAS, and fortunately, satisfactory results (hydrogen production and sludge reduction) had been achieved from this work. Compared with our previous works, MECs directly fed with fermented sludge, was simplified, cost-effective, and efficient.[19, 20] Compared with the research of Sun et al.,[40] we had separated soluble organic matters (soluble protein, soluble carbonhydrate and VFAs, especially VFAs) accumulation stage (AD process) from hydrogen production stage (MECs), the former, hydrolysis and acidification stage, could provide the primary substrate for MECs to produce hydrogen. Meanwhile, in MECs, could achieve the syntrophic interactions obtained in the research of Sun et al.. [40] And better performance achieved in our work had verified the positive effects of separated process. Compared with the research of Lu et al., [41] we had investigated the possibility of high-solid WAS as the substrate for AD-MECs process. And according to our previous study, [19, 20] the operation time of AD-MECs process had been shortened, but better performances had been achieved, in addition, the sludge reduction had been investigated.

The better performances of the process proposed in this work might be that, on one hand, the pretreatment methods used were more effective for WAS hydrolysis and acidification, and then the hydrogen production of MECs was enhanced, on the other hand, the fermented WAS in MECs could further extend the anaerobic fermentation, which might form synergy effects between fermentation bacteria and bio-hydrogen bacteria, as the latter could easily use metabolites from the former to produce bio-hydrogen, then the bio-hydrogen production was improved. Thus, the proposed process in this work for bioenergy recovery and sludge reduction was of great significance, and had application potential. However, this study just researched effects of AD-MECs process on performances of WAS reduction and bioenergy recovery. In the future, further study should be conducted to better understand the microbial response mechanisms of AD-MECs, while feeding with pretreated sludge, which was of great significance to gain insight into the proposed technology.

4. Conclusions

In this work, the pretreatment coupled with AD-MECs were set up for bioenergy recovery and sludge reduction. Several interesting conclusions can be achieved as follows: (1) The maximum sludge reduction achieved in heat-alkaline pretreatment, 36.9% and 46.7% for TSS and VSS removal, respectively. Sludge reduction of both heat-alkaline and ultrasonication pretreatments all met the USEPA standard. (2) MECs fed with fermented WAS, displayed positive potential for energy recovery, and the highest hydrogen yield and energy efficiency were 20.30 mgH_2/g VSS and 129.8%, respectively, obtained in heat-alkaline pretreatment. (3) Kinetic models, built on linear regression techniques, indicated that with initial concentrations of soluble organic matters increased, the bio-hydrogen yields of MECs increased linearly ($R^2 = 0.8903 \sim 0.9742$). (4) The pretreatment coupled with AD-MECs process can not only enhance sludge reduction, but also improve bio-hydrogen production, suggesting a promising technology for WAS treatment.

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Table 1. Characteristics of pretreated WAS after 3-day anaerobic digestion

	pH	VFAs (mg COD/L)	Carbohydrate (mg COD/L)	Protein (mg COD/L)	SCOD (mg COD/L)
	Ave. ±St. Dev.	Ave. ±St. Dev.	Ave. ±St. Dev.	Ave. ±St. Dev.	Ave. ±St. Dev.
Control	6.86 ±0.05	416.60 ±45.65	13.66 ±1.23	105.45 ±34.22	613 ±67
Heat-alkaline	7.93 ±0.17	1833.31 ±180.87	474.37 ±45.33	1514.57 ±143.22	4514 ± 123
Freeze-thaw	6.76 ±0.15	1039.36 ±54.33	52.93 ±10.32	453.44 ±86.03	1854 ± 56
Ultrasonicationation	6.47 ±0.23	1507.74 ±98.23	221.96 ±14.67	794.32 ±56.00	3012 ± 150

Note*: St. Dev. is standard deviation. And ave. is average.

Figure captions

Fig.1 Potential technique for waste activated sludge treatment

Fig.2 Performance of anaerobic fermentation and MECs start-up. (a) Percentage distribution of VFAs of pretreated WAS after anaerobic fermentation, (b) Performance of MECs start-up fed with acetate.

Fig.3 Performance of AD-MECs on sludge reduction. (a) TSS and VSS changes after AD-MECs process, (b) removal efficiencies and reduction rates of TSS and VSS.

Fig.4 Biohydrogen production and energy recovery by AD-MECs process fed with fermented WAS (a) Biohydrogen production, (b) energy efficiency.

Fig.5 Mathematical models. (a) Relationships between initial concentrations of soluble organic matters (soluble protein, carbohydrate and VFAs) and biohydrogen yields, (b) Relationships between TSS and VSS reduction rates and biohydrogen yields.

Fig.1

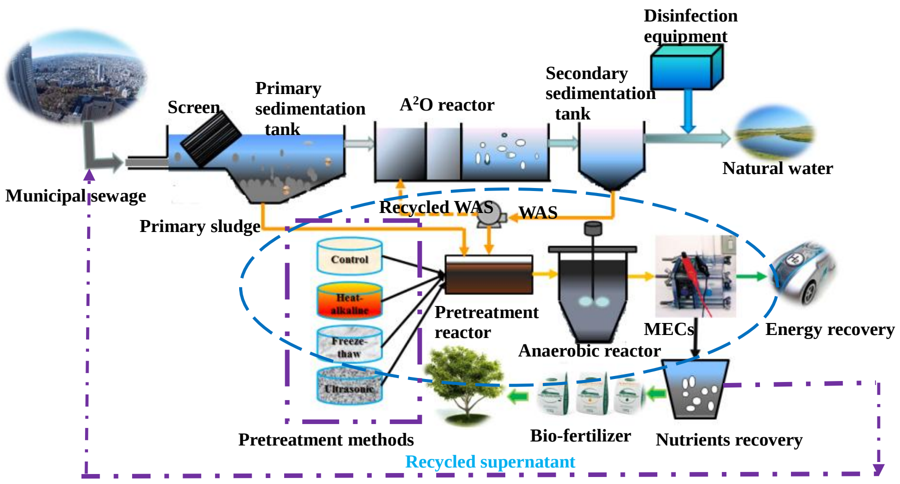

Disinfection equipment
Secondary sedimentation tank
Primary sedimentation tank
Screen
A^{2}O reactor
Natural water
Municipal sewage
Primary sludge
Recycled WAS
WAS
Control
Heat-alkaline
Freeze-thaw
Ultrasonic
Pretreatment reactor
Anaerobic reactor
MECs
Energy recovery
Bio-fertilizer
Nutrients recovery
Pretreatment methods
Recycled supernatant

Fig.2

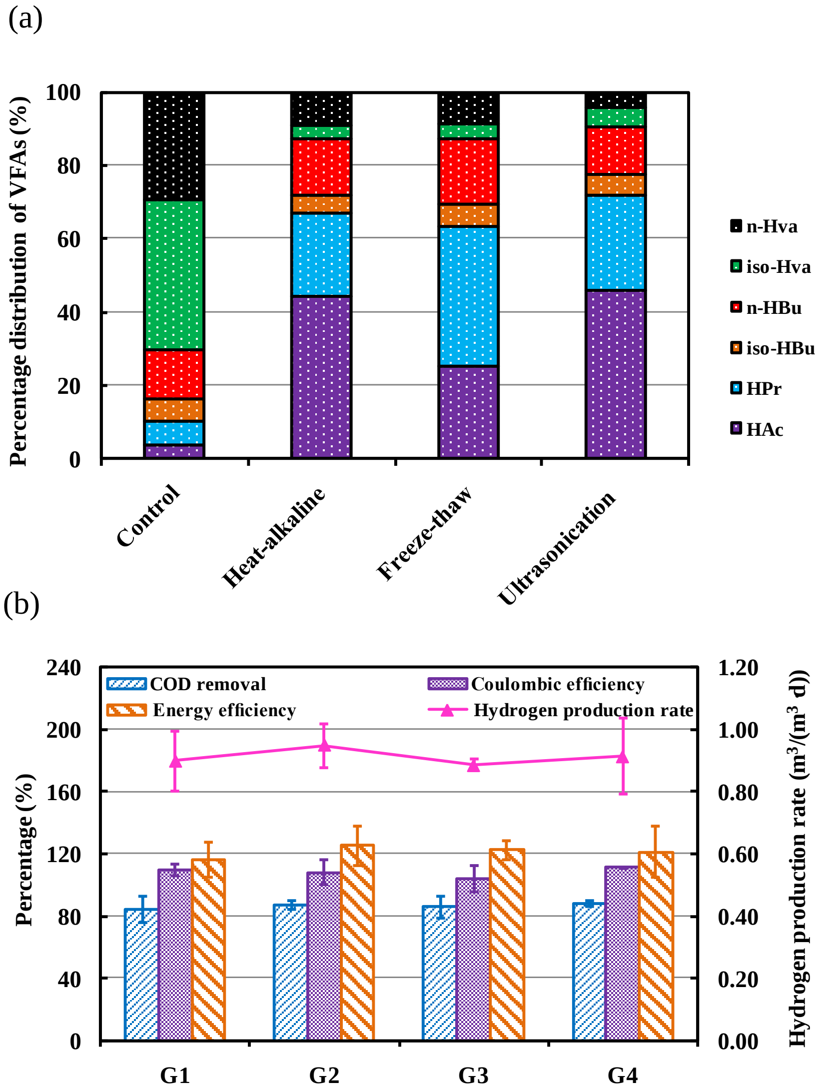

(a)
Percentage distribution of VFAs (%)
100
80
60
40
20
0
Control
Heat-alkaline
Freeze-thaw
Ultrasonication
n-Hva
iso-Hva
n-HBu
iso-HBu
HPr
HAc
(b)
Percentage (%)
240
200
160
120
80
40
0
COD removal
Coulombic efficiency
Energy efficiency
Hydrogen production rate
Hydrogen production rate (m3/(m3 d))
1.20
1.00
0.80
0.60
0.40
0.20
0.00
G1
G2
G3
G4

Fig.3

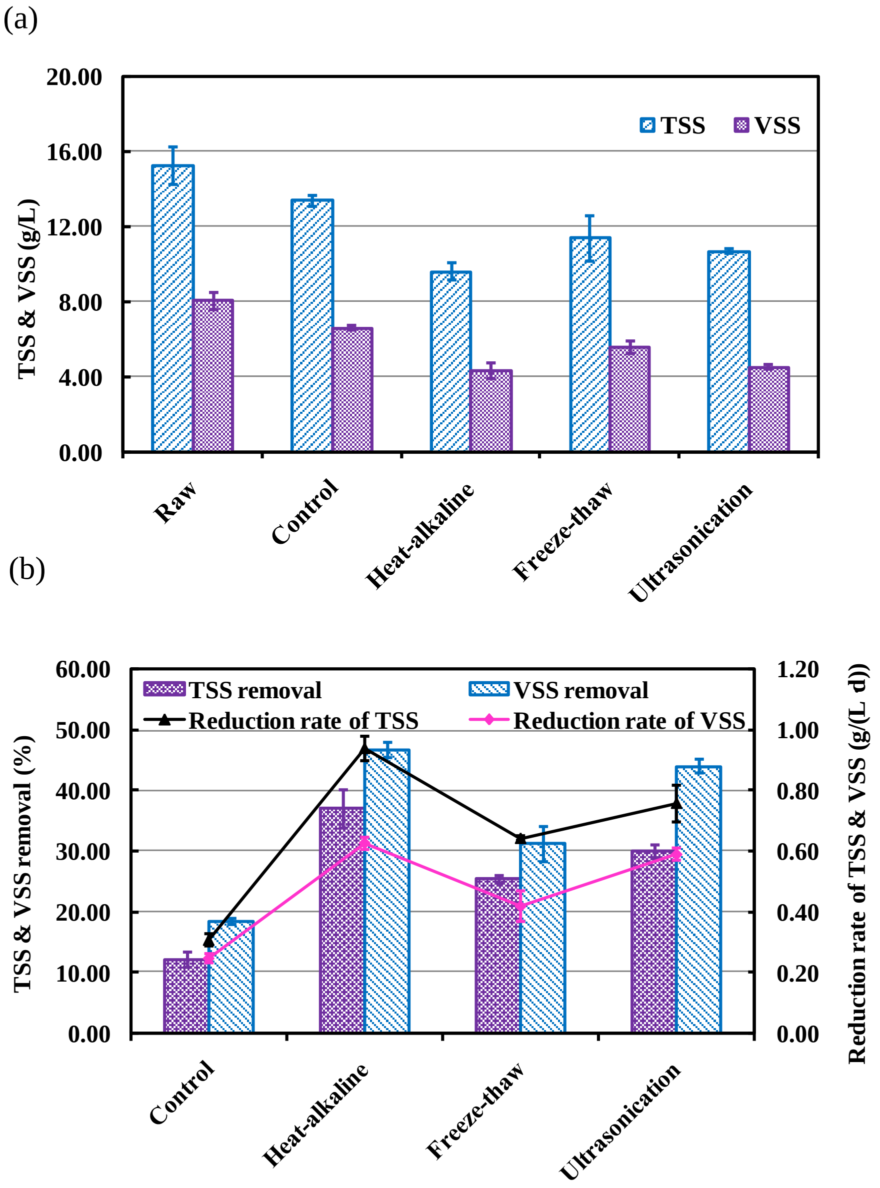

(a)
20.00
16.00
12.00
8.00
4.00
0.00
TSS & VSS (g/L)
▨ TSS
▩ VSS
Raw
Control
Heat-alkaline
Freeze-thaw
Ultrasonication
(b)
60.00
50.00
40.00
30.00
20.00
10.00
0.00
TSS & VSS removal (%)
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Reduction rate of TSS & VSS (g/(L d))
TSS removal
VSS removal
Reduction rate of TSS
Reduction rate of VSS
Control
Heat-alkaline
Freeze-thaw
Ultrasonication

Fig.4

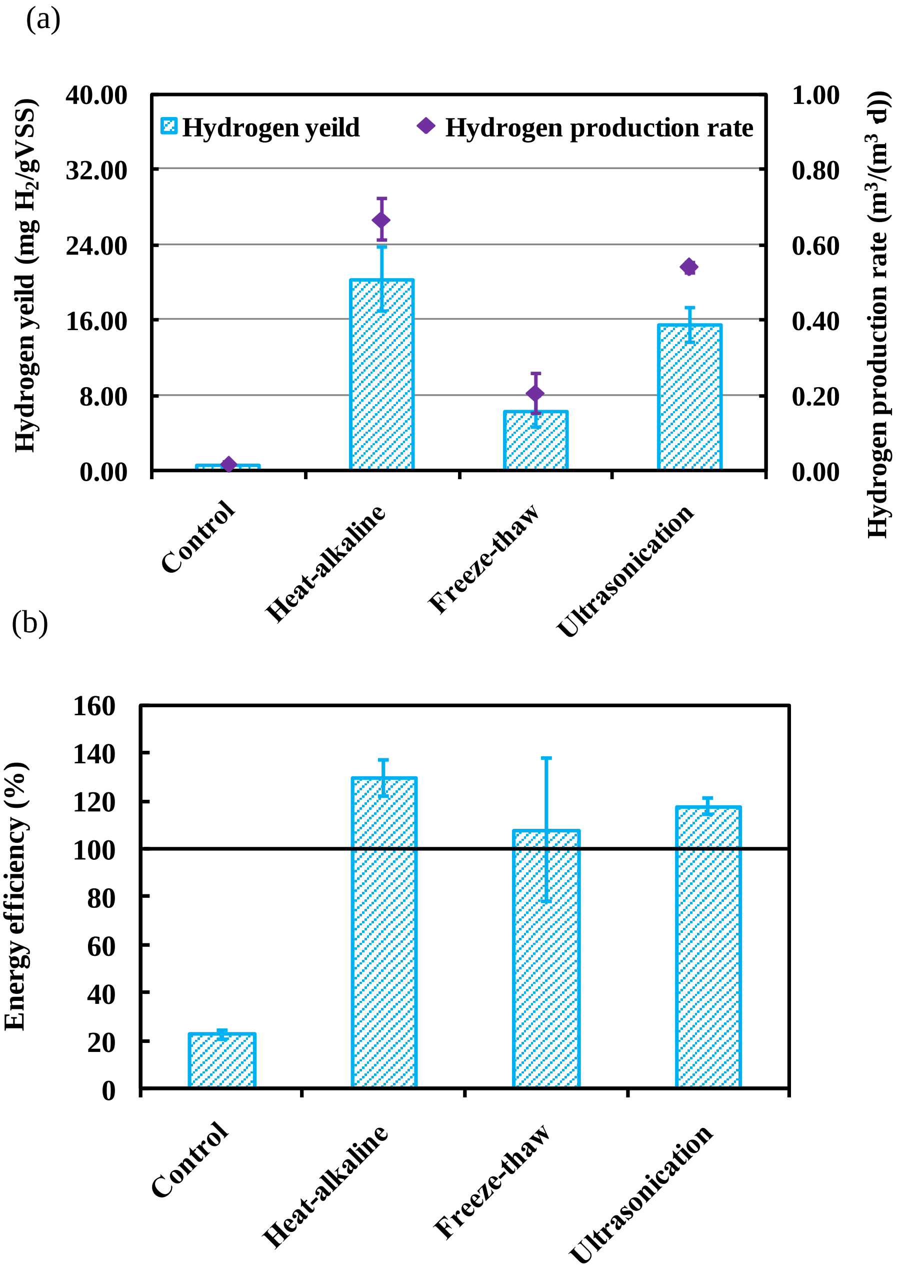
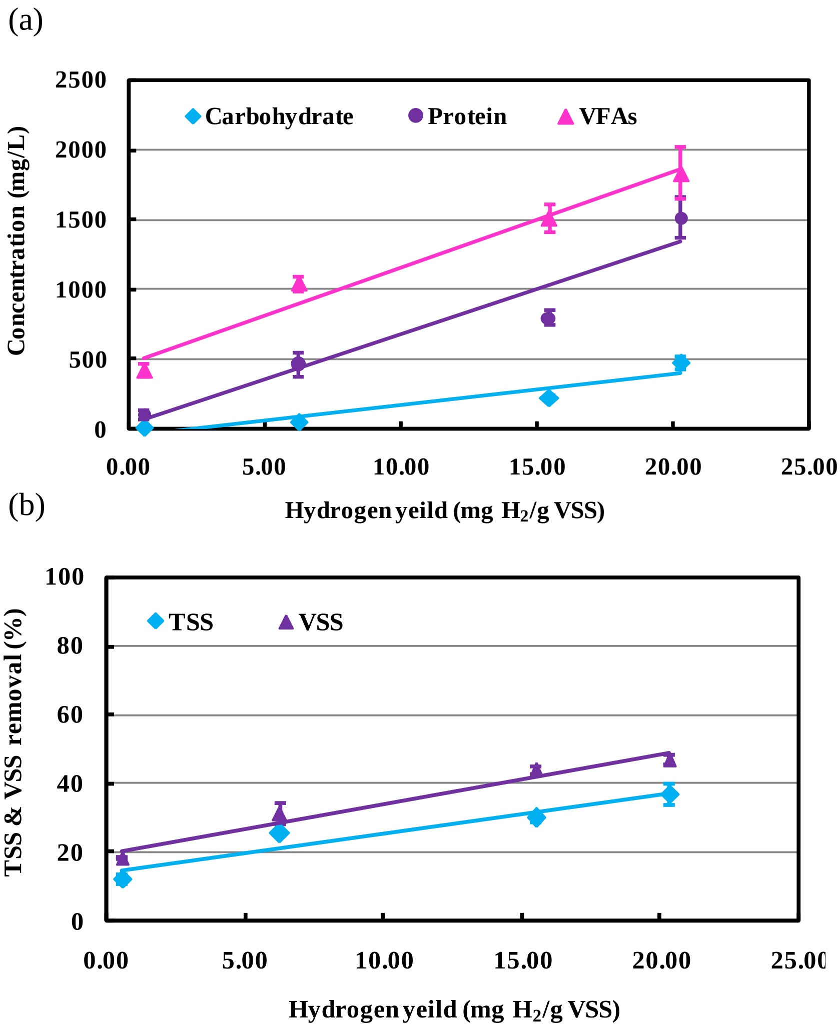

(a)
Hydrogen yeild
Hydrogen production rate
Hydrogen yeild (mg H_2/gVSS)
40.00
32.00
24.00
16.00
8.00
0.00
1.00
0.80
0.60
0.40
0.20
0.00
Hydrogen production rate ($m^3/(m^3$ d))
Control
Heat-alkaline
Freeze-thaw
Ultrasonication
(b)
Energy efficiency (%)
160
140
120
100
80
60
40
20
0
Control
Heat-alkaline
Freeze-thaw
Ultrasonication

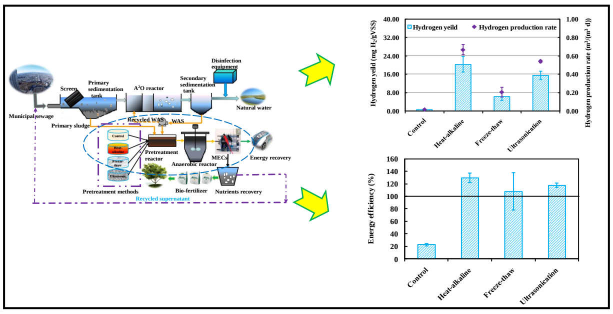
Fig.5


(a)
Carbohydrate
Protein
VFAs
Concentration (mg/L)
0
500
1000
1500
2000
2500
0.00
5.00
10.00
15.00
20.00
25.00
Hydrogen yeild (mg H_2/g VSS)
(b)
TSS
VSS
TSS & VSS removal (%)
0
20
40
60
80
100
0.00
5.00
10.00
15.00
20.00
25.00
Hydrogen yeild (mg H_2/g VSS)

Highlights:

A novel and attractive technology for renewable bioenergy recovery from WAS and sludge reduction has been investigated.

Color Graphic:



Highlights:

A novel and attractive technology for renewable bioenergy recovery from WAS and sludge reduction has been investigated.

Color Graphic: