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Enhanced biohydrogen production from waste activated sludge in combined strategy of chemical pretreatment and microbial electrolysis

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ABSTRACT

Cascade conversion methods are required to treat waste sludge (WAS) targeting at abundant biomass embedded in its cells and extracellular polymer. Two limiting factors have to overcome to obtain efficient conversion: (i) low release of soluble organics in raw WAS; (ii) limited conversion rate from organics to energy. Combined strategy of effective chemical pretreatment and microbial electrolysis was tested. Four kinds of chemicals (SDS, NaOH, peracetic-acid and β -cyclodextrin) were chosen to enhance volatile fatty acids (VFAs) production and following effects on hydrogen production and energy recovery by microbial electrolysis was further studied. The highest VFAs concentration was accumulated to 4712.69 mgCOD/L by β -CD within 3 days, which was increased to 4 times of unpretreated WAS. Other three chemicals respectively achieved ~2.5-fold increase by SDS and PAA, and ~2-fold increase by NaOH. However, the highest hydrogen yield was 8.5 mgH₂/gVSS with energy efficiency of 138% \pm 8% by SDS pretreatment. The pretreatment substantially affects VFAs components, reflected on cascade changing of current and hydrogen production rate. The cascade conversion indicated that accumulation of acetate and propionate in SDS pretreatment benefited the most hydrogen production in combined strategy.

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Introduction

With rapid development of waste water treatment plants, huge production of waste activated sludge (WAS) was causing more attention and was urged to dispose and reduce [1]. The disposal of the WAS also caused a challenge for its high treatment cost which took up ~60% of the operation costs of a plant [2]. Actually, WAS is regarded as a potential biomass energy source for its high content of organic matter [3,4]. Relevant researches had worked on converting WAS into biogas, fertilizer, or carbon source, which made profits to reduce costs for WAS disposal [5]. Among various energy recovery methods, more attention had been paid to anaerobic sludge fermentation for its potential to transfer organic matter into biogas (60–70 vol% of methane) [6]. However, the traditional anaerobic fermentation struggled for a long reaction time and low utilization efficiency of raw WAS with only 30–50% of the total COD (or volatile solids) degraded in 30 days [7].

Recently, microbial electrolysis cell (MEC) has been developed as a promising way for hydrogen production from organic wastes, and MEC achieved high purity hydrogen (>90 vol% of hydrogen) with a small external voltage (0.2–0.8 V) [8–10]. Hydrogen production rate was successfully up to 3.12 m³/m³reactor/d under 0.8 V external voltage when feeding with acetate in single chamber MEC. For overall system, input energy was evaluated as a small part of combustion lose equaled to 0.5 m³ hydrogen/m³reactor [9]. The energy yield of hydrogen was 2.57 times than methane. It looks much more valuable to get hydrogen as a promising energy with completely harmless and high heat value from waste sludge [11,12].

The WAS is composed of protein (35–61% of the total chemical oxygen demand (TCOD)), carbohydrates (7–11% of TCOD) and other component (<1% of TCOD). However, most of biomass in raw WAS was contained inside the cell and most of them were macromolecule which lead to low biodegradation. The VFAs was more easily to be utilized compared to other components in WAS for MEC microorganism. The hydrogen production efficiency was 60.83 mmol-H₂/g-COD feeding with the acetic in a single chamber MEC [13] and the maximum hydrogen production efficiency was only 21.5 ± 0.2 mmol-H₂/g-COD when protein was the only substrate [14]. Hence, efficient pretreatment methods should be implemented to overcome these limitations and release more available organic matters for further process. Although chemical, physical, biological and other joint pretreatment methods were used to pretreat WAS [6,15], chemical pretreatment was reasonably applied to enhance VFAs accumulation with low energy input (low cost) and quick reaction [3,16–20]. It is practically to consider a benefit effect on both accumulation of soluble organics and H₂ production in MECs, including conductivity, buffer capability (pH) and inhibition to bioelectrochemical system [21,22]. In previous studies, the components of the WAS fermentation products were substantially influenced by specific chemical addition [16,17,19], thereby the following H₂ production was affected in MECs. The utilization order was found differently among VFAs, carbohydrates and protein in previous study using ultrasonic pretreatment [12,23], indicating the importance to figure out the biodegradation

regulation from WAS to biogas in MECs. However, there were few reports to further disclose the characteristics of cascade bioconversion related to electron recovery in mixed carbon sources for microbial electrolysis.

In this study, four kinds of chemical pretreatment reagents were chosen to enhance WAS hydrolysis. Respectively, they were (1) oxidant (acid), like peracetic-acid (PAA) [18], (2) alkaline, like NaOH [3], (3) lysis, like sodium dodecyl sulfate (SDS) [17], (4) biosurfactant, like β -cyclodextrin (β -CD) [16]. Experiments were proceeded to find out the optimum reagent both for WAS hydrolysis and biodegradation in MEC. The hydrogen production and energy recovery was discussed through different pretreatments. The degradation rules of the substrates in pretreated WAS were analyzed in microbial electrolysis process.

Material and methods

Chemical pretreatment and fermentation of WAS

Waste sludge was collected from the secondary sedimentation tank of Wenchang municipal WWTP in Harbin, China. The sludge was concentrated by settling for 24 h and moving the water layer away then stored in the refrigerator at 4 °C. The large particles were wiped out through the 40 mesh sieve. The characteristics of concentrated WAS are played in Table 1. The VSS of WAS was adjusted to 14 g/L before use. The optimum dosages of four kinds of chemicals (SDS, NaOH, peracetic-acid and β -cyclodextrin) were determined reference to reported studies (Table 2).

The combined strategy of chemical pretreatment and MEC was carried out in two stages. First stage was WAS fermentation with chemical pretreatment in ten glass bottles (500 mL, Sichuan Shubo CO., China). After adding the chemicals and 350 mL WAS, all bottles were flushed with nitrogen gas for 10 min to remove oxygen. The bottles were stirred in an air-bath shaker at 35 ± 2 °C for 3 days to enhance the VFAs accumulation. The second stage was biohydrogen production by feeding with supernatant of WAS in the MEC reactors. The supernatant which was sludge fermentation liquid (SFL) after WAS fermentation 3 days was separated by centrifugal separation at 10,000 rpm.

MECs reactor setup and operation conditions

Fifteen single chamber MEC reactors were set up as previous studies [12]. Effective volume was 40 mL, including a 28 mL

Table 1 – Main characteristics of the concentrated WAS.

| Parameter | Value |
|---------------------------------------|----------------|
| TSS (Total suspended solids) | 37.53 g/L |
| VSS (Volatile suspended solids) | 24.79 g/L |
| SCOD (Soluble chemical oxygen demand) | 408 mg/L |
| TCOD (Total chemical oxygen demand) | 11880 mg/L |
| VFAs (Volatile fatty acid) | 221.34 mgCOD/L |
| Carbohydrate | 11.89 mgCOD/L |
| Protein | 0.00 mgCOD/L |
| pH | 6.89 |

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