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Effective hydrogen production using waste sludge and its filtrate

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ABSTRACT

Waste activated sludge from a wastewater treatment plant is rich in polysaccharides and proteins and thus is a potential substrate for producing hydrogen. In this study, the hydrogen yield could be largely enhanced by using filtrates of waste sludge. The hydrogen yield was effectively increased from 1.34 mg H_2/gTCOD (waste sludge) to 4.44 mg H_2/gTCOD (filtrate). The changes of nutrients such as SCOD, protein and carbohydrate in sludge and its filtrate during fermentation have obviously diversity. It implied that the nutrients could be further released from the solid phase of the sludge during fermentation. In addition, the fermentation of the sludge was advantageous for releasing nutrients, but the H_2 production might be lower at high substrate concentrations as a result of the inhibition products formed during hydrogen production. Therefore, the solid phase of waste sludge could not be utilized by the anaerobes as nutrient and it might absorb certain products, release toxic metals or deliver toxic substances during fermentation. The changes of pH indicated that conditions were favorable for hydrogen production from the filtrate. The 16S rRNA gene sequence, phylogenetic and biochemical character analyses demonstrated that strain GZ1 was a new strain of *Pseudomonas* and suitable for hydrogen production.

1. Introduction

Owing to finite resources and emission of pollutants, hydrogen is a promising alternative to fossil fuels. Hydrogen is a clean energy that produces water instead of greenhouse gases when combusted. Furthermore, hydrogen has a high-energy yield (142.35 kJ/g) that is about 2.75 times that of hydrocarbon fuels [1]. Biomass (microbes, plants, animals, and their organic waste products) provides approximately 14% of the world's energy needs. Unused, discarded biomass residues are a potential energy resource, which at present are not well managed and thus pose significant environmental problems [2]. With the development and commercialization of fuel cells, hydrogen production from biomass is also considered as an alternative energy source in a decentralized power generation scenario [3]. When coupled to the treatment of wastes, this process is able to solve two problems: the reduction of pollution from the uncontrolled degradation of waste and the generation of a clean alternative fuel [4].

In 2001, about 4.22 billion tonnes of municipal wastewater were treated in China, producing about 0.55–1.06 million tonnes of dry sludge [5]. Waste activated sludge from a wastewater treatment plant is rich in polysaccharides and proteins and thus represents a potential substrate for producing hydrogen [6]. The volume and mass of sludge produced from wastewater plants increase annually. The treatment and disposal of the sludge from municipal, as well as industrial wastewater plants have become complex management/environmental issues [7]. The hydrolysis of the microbial cells limits the speed of the anaerobic digestion of sludge and results in a long HRT [8,9]. To improve the anaerobic digestion of waste sludge, the most logical approach is to disrupt the microbial cells of sludge. Due to low hydrogen yield from the raw sewage sludge, a number of pretreatment approaches have been investigated in previous studies [10–13]. Hydrogen yield was improved to 1.4 mgH_2/gDS and 1.5–2.1 mmolH_2/gCOD using boiled sludge [12]. It was also produced 1.34 mg H_2/gTCOD with sterilization pretreated sludge in our previous study [13]. This value is comparable to that of protein fermentation, but is still far lower than that of polysaccharides.

Until recently, there was little information regarding the use of filtrate to produce hydrogen and the influence of solids in waste sludge in hydrogen production was unclear. In this study, the changes of nutrients (SCOD, protein and carbohydrate) of both sludge and its filtrate during fermentation were demonstrated for the first time, and the influence of the solid phase on hydrogen production from waste sludge was also analyzed. The experimental results indicated that fermentation of the filtrate could produce a higher bio-hydrogen yield than that of waste sludge.

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Table 1
The characteristics of waste sludge used in this study.

Parameter	Raw sludge	Pretreated sludge	Filtrate
TCOD(mg/L)	13,050 ± 2530	16,000 ± 2750	3455 ± 705
SCOD(mg/L)	380 ± 60	2840 ± 25	2011 ± 12
pH	6.9 ± 0.2	7.3 ± 0.2	7.8 ± 0.4
Carbohydrate(mg/L)	27 ± 7	203 ± 32	446 ± 43
Protein(mg/L)	33 ± 5	223 ± 21	351 ± 28
Cu(mg/kgDS)	443.2 ± 3.9	NA	19.0 ± 0.2
Pb(mg/kgDS)	110.7 ± 19.0	NA	24.7 ± 15.7
Cd(mg/kgDS)	18.8 ± 0.4	NA	0
Zn(mg/kgDS)	779.3 ± 7.9	NA	0
Ni(mg/kgDS)	49.8 ± 2.6	NA	4.8 ± 3.9

NA: not analysis; DS: dry sludge.

2. Materials and methods

2.1. Substrate

Waste sludge was taken from the recycled stream of the secondary treatment stage of a Municipal Wastewater Treatment Plant in Changsha which handled 140 000 m^3 wastewater daily. The pH value of the sludge was 6.9 ± 0.2. The SS (suspended sludge) and VSS (volatile suspended sludge) were 14.63 g/L and 8.28 g/L respectively. The collected waste sludge was pretreated by sterilization for 20 min at 121 °C (Hirayama manufacturing corporation, HV-50, Japan). The filtrate was obtained from filtering the solid matter of pretreated sludge through centrifuge at 4000 rpm. Both the sludge and its filtrate were the substrates in the fermentation tests. Table 1 lists their characteristics. The TCOD for the sludge was much higher than filtrate, indicating that most organic compounds in the sludge sample were in an insoluble form.

2.2. The inoculum

A *Pseudomonas* sp. GZ1 (EF551040) was used as seed bacteria. The inoculum was isolated from the anaerobic granular sludge which was collected from Yueyang paper mill. The applied purified procedures include: (1) Heat pretreatment at 80 °C for 2 h to inactivate the methanogenic bacteria. (2) Crushing down the granular sludge using sterilized apparatus. (3) Isolating and purifying the incubated sludge on solid culture medium first by Hungate method [14] and about three days later transferring the colonies to a liquid culture medium. These procedures were repeated three times. (4) The preliminary hydrogen production was tested, and the strains with the highest hydrogen yields were used as the inoculum in this study. The strain used in this study was analyzed using the following steps: DNA extraction; PCR amplification of 16S rDNA gene [15]; PCR purification and 16S rRNA sequence analysis. The results showed that strain GZ1 is a member of the *Pseudomonas* family, named as *Pseudomonas* sp. GZ1. The registration number was EF551040, and it was accessible in GenBank. The superficial structure of bacteria was observed by field emission scanning electron microscope (SEM) (TSM-1230, Japan). The size, capsulate and flagellum were observed by transition electron microscopy (TEM) (TSM-6360, Japan). Phylogenetic trees were constructed by the neighbor-joining method using the MEGA version 3.1 packages. Bootstrap analyses for 1000 replicates.

2.3. Batch fermentation and testing

Substrate (100 ml) was mixed with 5 ml of inoculum suspension and was anaerobically (sparged with N_2 for 10 min) incubated at 35 °C in 250 ml serum bottles with a reciprocal shaker operated at 125 rpm. The bottles were capped with silica gel stoppers. The overall schematic of the hydrogen production reactor is shown in Fig. 1. The COD, protein, carbohydrate, pH and VFAs (volatile fatty acids) were measured every 2–4 h throughout fermentation. The concentration and yield of H_2 were measured every 1–4 h during fermentation. Under identical conditions, three fermentation bottles were analyzed and the average of their data along with standard deviation was reported to account for possible errors introduced as a result of sampling procedure or inherent sample variability.

VFAs and H_2 were measured with a gas chromatograph (Agilent Technologies 6890 N, USA) [13]. The TCOD (total chemical oxygen demand) of the sludge was measured by the microwave digestion method (model MS-3 Microwave Digestion System for COD Determination, China). The SCOD (soluble chemical oxygen demand) of the sludge sample was obtained after filtering through a 0.45 μm membrane. SS (suspended sludge) and VSS (volatility suspended sludge) were determined by standard method [16]. The pH was measured with a digital pH-meter (pH315i, WTW 82362 weilheim, Germany). Protein and carbohydrate were determined by their respective standard method [15]. The correlation analysis was carried out using SPSS 11.5 (SPSS Inc., USA).

3. Results and discussions

3.1. The changes of SCOD and SCOD/TCOD

Before fermentation, the ratio of SCOD/TOCD was only 2.91% in the raw sludge. After pretreatment, the SCOD/TOCD increased to 17.75%. For the filtrate, the SCOD/TCOD was 58.21% much higher than the sludge. In addition, the changes of SCOD and SCOD/TCOD using the filtrate gradually decreased with time, different from the change of SCOD/TCOD using the sludge during hydrogen production (Fig. 2). The SCOD of the filtrate decreased from 2011 mg/L to 950 mg/L, and the SCOD/TCOD decreased 12%. On the contrary, both SCOD and SCOD/TCOD of the sludge increased, and the same

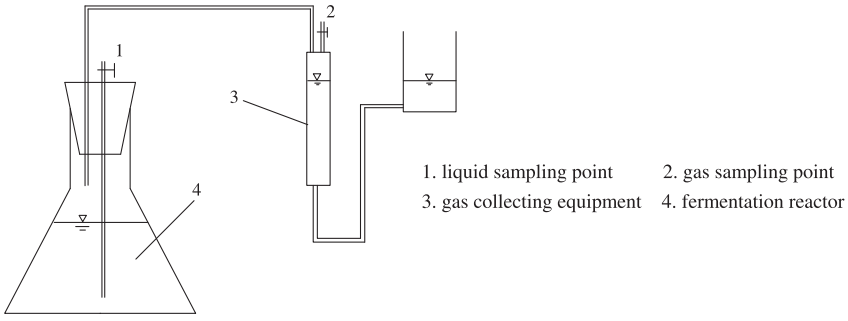

Fig. 1. Overall schematic of the hydrogen production reactor.