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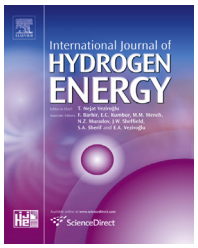

Hydrogen and methane production in a bio-electrochemical system assisted anaerobic baffled reactor

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ABSTRACT

In this study, a new process was proposed to enhance the stability and efficiency of an anaerobic baffled reactor (ABR). The process was examined in a four equal compartments ABR with total volume of 3.46 L. The first compartment was operated for fermentative hydrogen production and the last three compartments were used as continuous singer chamber microbial electrolysis cells (MECs) for methanogenesis. The system was operated at 35 ± 1 °C and hydraulic retention time (HRT) of 24 h with influent chemical oxygen demand (COD) concentration of 3500 mg/L–4000 mg/L. The results indicated that the proportion of hydrogen in the first compartment was 20.7% and proportions of methane in the last three compartments were 98.0%, 93.6% and 70.1%, respectively. A total of 98.0% of COD removal rate was achieved as well. Hence, this new system has following advantages: hydrogen production with cleaner effluent, high COD removal rate, and net methane production for practical use.

Introduction

Hydrogen production in dark fermentation is a renewable way to convert waste organics to clean energy. Kraemer et al. [1] reported that there was a remain 66.0% substrate electrons in the fermentation products of volatile fatty acids (VFAs); Antonopoulou et al. [2] found that total COD removal rate was below 5.0% with proportion of 29.3% hydrogen production. To facilitate the requirement of effluent COD concentration, methanogenesis is needed to convert VFAs into methane [3]. Acidogens and methanogens can coordinate with each other by providing proper nutritional and physiological environment.

The anaerobic baffled reactor (ABR), originally developed by Bachman and Mccarty, can be considered as a series of up-flow anaerobic sludge bed (UASB) reactors that still play significant role within the field of wastewater treatment plants [4,31]. The fundamental point of enhancing the stability and efficiency of an anaerobic process with high hydrogen production rate, is to efficiently degrade acidogenic intermediate

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metabolites into methane. Nevertheless, fermentative acidogens usually grow faster than methanogens and moreover the methanogens are sensitive to environmental conditions such as pH and hydrogen partial pressure [5,6]. This may result in the accumulation of VFAs, and consequently inhibiting the methanogenesis and causing the system unbalanced [7]. Florencio et al. [8] observed that VFAs accumulation in the condition of continuous acetogenesis from methanol at organic loading rates of 21 g COD/L d resulted in poor COD removal rate of 16.3%.

Thus, it is desired to develop a novel process of new anaerobic metabolic pathway that could degrade organic matters more efficiently. In the mean time, many researchers have reported that the production of methane in singer chamber microbial electrolysis cell (MEC) [9,10]. Clauwaert and colleges [9] investigated that one mole acetate can be converted into 0.41 mol methane at the temperature of 22–28 °C in the biocatalyzed electrolysis. Alternatively the intermediate metabolite of ABR system can be used as substrates of electrolysis process since the substrates such as VFAs used in electrolysis to produce methane are obtained uneconomically.

Thus the authors' proposed technique of an ABR combined with MECs might be a possible new way for hydrogen and methane production with cleaner effluent. In this study, well domesticated electrode films with power suppliers into the last three compartments out of four compartments ABR are formed as three continuous singer chamber MECs. The first compartment of ABR still acts as hydrolysis and fermentation stage. The objectives of this study are as follows; (i) to confirm the suitability and effectiveness of the new combined process under the accumulation of VFAs and inhibition of traditional methanogens, (ii) to investigate the reasons of its function preliminary, and (iii) to identify the other possible effects resulted from this combined process.

Materials and methods

The configuration of the new system and domestication of electrode films

The ABR was operated with continuous flow and was made of plexiglass with a volume of 3.46 L of the following dimensions: 24 cm × 8 cm × 18 cm (L × W × H). It was divided into four equal compartments by vertical baffles as shown in Fig. 1. Each compartment was divided into down-comer and up-comer regions by hanged baffles of 45° edge with the length of 1.20 cm and 4.80 cm respectively. The anode and cathode films were fixed in the up-flow region of each last three compartments and connected with external power supply through titanium wire. The anode film was 60.00 cm^2 with 6.00 cm wide and 10.00 cm long. Before the anode films were fixed into the compartments of ABR, they were enriched with microorganisms of electrochemical activity in a microbial fuel cell (MFC) while the cathode films were made of stainless steel mesh catalyzed by Ni nanoparticles. And the modified method of Middaugh [11] was used for the catalysis process. Diffusion and catalyst layers were made on each side of the stainless steel mesh. On the diffusion layer side, the

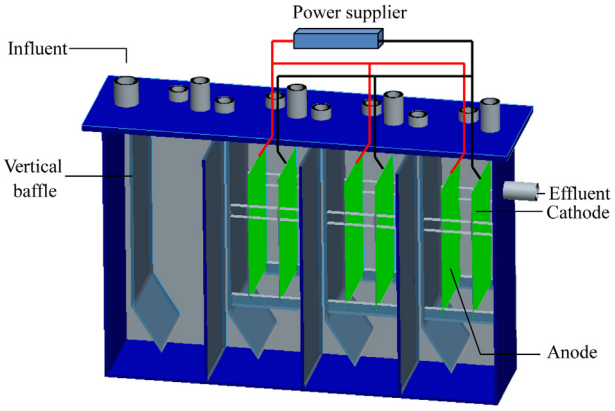

Fig. 1 – The structure of anaerobic baffled reactor combining with microbial electrolysis cells.

stainless steel mesh was painted with the PTFE (wt60%) uniformly and dried at 350 °C for 10 min. And it was reduplicated for four times. On the catalyst layer side, the stainless steel mesh was added with the Ni nanoparticles that obtained with dissolving 120 mg of Ni nanoparticles in 99.6 μL of DI water, 399.6 μL pure isopropanol and mixing with 800.3 μL PTFE (wt60%) solution, following the vortex for 0.5 min [11]. Finally, the cathode film was put into the muffle furnace at 350 °C for 10 min. One g/L sodium acetate was added as carbon sources and 50 mM of phosphate buffer nutrient medium was used to sustain the pH value of 7.00 in the MFC as the method described by the Wu et al. [12]. After 60 days of domesticating, the voltage generated by the MFC remained at stable state. The last three compartments of the ABR were created an oxygen-free environment after fixing the anode films and cathode films into it by the experiment of nitrogen blow-off for 20 min. The operating temperature was 35 ± 1 °C and the hydraulic retention time (HRT) was 24 h. A working potential of 0.9 V in the MECs was employed. The anaerobic microbial cultures used in the study were collected from secondary settling tank of the wastewater treatment plant in Xiamen.

Wastewater composition

As a primary substrate providing a COD to the required concentration glucose was added to the wastewater. And a mineral medium of 1 mL/L concentration was also added as a nutrients. It was prepared by dissolving 50 mg/L H_3BO_3, 30 mg/L $CuCl_2$, 50 mg/L $MnSO_4$, 50 mg/L $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 50 mg/L $AlCl_3$, 50 mg/L $CoCl_2\cdot 6H_2O$, 50 mg/L $ZnCl_2$, 50 mg/L $NiCl_2$ in distilled water. The proportion of COD:N:P was 500:5:1. $NaHCO_3$ was also added to the ABR to regulate the pH levels.

The operation of system

The system was operated into three stages: start-up stage (from 1st day to 14th day), regulation stage (from 15th day to 39th day) and combining stage (from 40th day to 56th day). In the combining stage, the well domesticated electrode films were added in the last three compartments. In the start-up