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Short communication

Improvement of bioelectrochemical property and energy recovery by acylhomoserine lactones (AHLs) in microbial electrolysis cells (MECs)

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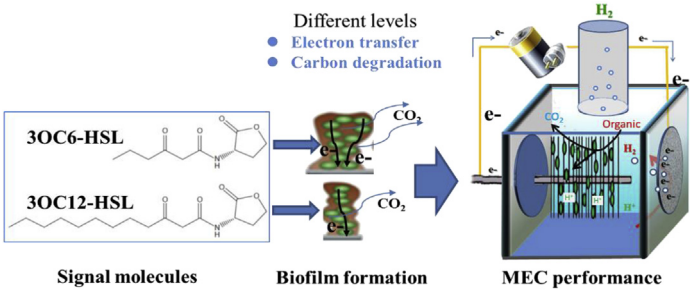
HIGHLIGHTS

- Acylhomoserine lactones enhanced bioelectrochemcial activities in MECs.
- MEC performances were affected by chain length and concentration of AHLs.
- Highest H_2 yield was achieved by 3OC6-HSL at an initial concentration of 10 μM.

GRAPHICAL ABSTRACT



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ABSTRACT

Quorum sensing (QS) has been extensively studied as a cell–cell communication system, where small chemical signal molecules (acylhomoserine lactones, AHLs) can regulate the bacterial communications in bioelectrochemical systems via chemical signaling and electric signaling. In this study, electrochemical activity of bio-anode is substantially promoted by adding two kinds of AHLs with different chain length at the stage of community formation in microbial electrolysis cells (MECs). Hydrogen yield increase is observed by adding of two chain length AHLs, 3-oxo-hexanoyl-homoserine lactone (3OC6-HSL) and 3-oxo-dodecanoyl homoserine lactone (3OC12-HSL). A higher MEC current is acquired with addition of 3OC6-HSL than 3OC12-HSL at a fixed voltage of 0.8 V (vs. SHE). The highest yield is up to 3.8 ± 0.2 mol H_2 mol^{-1} acetate at 10 μM 3OC6-HSL, which is increased 29% over control MECs. Evaluated on applied voltage, energy efficiency is increased to 171.6 ± 21.3% with short chain AHL, however, no significant improvement is performed on energy efficiency and coulombic efficiency with long-chain AHL. The study shows that bioelectrochemical characteristics of MECs varied on the chain length of AHL signal molecules and short-chain AHLs have a more positive effect on electron transfer and energy recovery in MECs.

1. Introduction

Quorum sensing (QS) signal molecules regulate the behavior of microbial organisms and directly facilitate microbial survival by promoting an advantageous lifestyle within a given environmental niche [1]. QS is a widespread phenomenon in microbial communities that employs autoinducing chemical signals to coordinate cooperative activities including biofilm formation [2,3] and extracellular enzyme secretion [4]. Recent works revealed that QS plays crucial roles in wastewater treatment on controlling the biological

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processes associated with biodegradation and bioelectrochemical activities [5]. The production of acylhomoserine lactones (AHL) or AHL-like molecules was observed in various biodegradation systems [3,6]. It was proved that significant amount of AHLs were produced by some bacteria like *Pseudomonas* sp. and thus QS regulation mechanisms were triggered to achieve a completely degradation on complex compounds [7]. Moreover, an enhanced electron transfer was manipulated by *rhl* AHL-mediated QS system, which has been verified in a pure culture accumulated microbial fuel cell (MFC) [8].

As a novel green energy technology, microbial electrolysis cells (MECs) have been proposed with great potential to degrade organic wastes and simultaneously recover energy for hydrogen generation as a sustainable energy carrier from waste with high efficiency [9–11]. The current studies has proved that MEC performed a higher energy recovery than MFC on over 90% coulombic efficiency and hydrogen yield from either simple organics or complex carbons [12]. Although various electron transfer mechanisms have been proposed [13–15], the efficiency of extracellular electron transfer is a major limiting factor that constrains the energy output in application of bioelectrochemical systems (BES). With the understanding that many anodic respiring bacteria related to proteobacteria can use AHLs as quorum-sensing signals [16], researches on QS activity have been directly carried out in MFCs, which have obtained positive effects on current generation by addition of signal molecules [8,17]. However, the signal effects vary in acyl group length and substitution depending on systems. Firstly, AHLs were much more significantly functioning on electron transport under anaerobic conditions without any oxidative stress [18]. However, potentially, hydrogen recovery in MEC requires a strict anaerobic/reductive condition, which was a different energy generation approach compared to MFCs under a microaerobic condition under air cathode [19]. Secondly, differences in acyl chain lengths are a factor in signal permeability. Short-chain acyl-HSLs, like *N*-3-oxo-hexanoyl-HSL (3OC6-HSL) or butanoyl HSL, can diffuse freely through the cell membrane. While still diffusible, long-chain acyl-HSLs like *N*-3-oxo-dodecanoyl-HSL (3OC12-HSL) appear to partition to the cell membrane [16]. Moreover, study showed that some bacteria were able to degrade long chain AHLs but not short chain AHLs as the sole carbon source [20].

The aim of the study was to investigate the energy recovery effects by addition of AHLs in MEC system. Two typical AHLs, short-chain acyl-HSL (3OC6-HSL) and long-chain acyl-HSL (3OC12-HSL), were taken to test effects on bioelectrochemical performance and energy recovery. The hydrogen yield and energy efficiency were discussed under different AHL concentrations at the beginning of MEC setup. To our knowledge, it is the first study to apply AHLs in MEC as a potential factor to improve the energy generation.

2. Material and methods

2.1. MECs reactor setup and operation conditions

Single chamber MEC reactors were set up with an effective volume was 38 mL, including a 28 mL chamber (3 cm diameter × 4 cm length) and a 10 mL gas collection tube as described in the previous study [21]. The anode was a graphite brush (3 cm diameter × 4 cm; 0.22 m^2 surface area) and while the cathode was made of carbon cloth (YW-50, YiBang; Taiwan) covered with a Pt catalyst layer (0.5 mg Pt cm^{-2} in one side) [22]. The reactors were operated in MEC model [19] and inoculated for two 24-h processes by mixture of PBS (50 mM; pH = 7.0; 1500 mg L^{-1} acetate) and wastewater (V:V = 50%:50%) from local Gaobeidian municipal WWTP in Beijing. Two typical AHLs of 3OC6-HSL and 3OC12-HSL were added in each inoculation process with two concentration levels of 1 μM and 10 μM respectively [2]. Triple reactors were applied in each condition and two for control without addition of any AHL. All reactors were applied with the same inoculum source of the wastewater for 24 h. The external voltage was applied as 0.80 V. The inoculation was repeated again with new addition of AHLs. After 48-h inoculation, all MEC reactors were refilled with PBS medium (50 mM; pH = 7.0; 1500 mg L^{-1} acetate) every 24-h and maintained for at least 10 cycles to get stable hydrogen yield at room temperature (25 °C).

2.2. Analysis and calculation methods

Cyclic voltammetry was performed from −0.6 to 0.0 V (vs. SHE) with a scan rate of 2 mV s^{-1} using saturated calomel reference electrode (SCE, model-217, Shanghai Precise. Sci. Instru. Co., Ltd., China; 0.247 V vs. standard hydrogen electrode). The currents were automatic monitored (Acquisition system; Keithley Instrument) through a 10 Ω resister. The gas was collected by a gas bag (50 mL; Cali5-Bond; Calibrated Instrument Inc) and gas components were analyzed by a gas chromatography (Fuli, GC9790; Zhengjiang instrument Inc, China) with a packed column [22] (TDX-01; 2 m length). The volume of generated gas was measured by a glass syringe. The VFAs were analysis by a gas chromatography (Agilent 4890; J&W Scientific, USA) with a capillary column (19095N−123HP-INNOWAX; 30 × 0.530 mm × 1.00 ìm; J&W Scientific, USA) [23].

The energy and coulombic efficiency were calculated to characterize the performance of MEC reactor [23]. Columbic efficiency indicated the recovery ability of electron, defined by the ratio of coulombs recovery to the total coulombs in substrate, which is integrated by current and time according to the equation $Q = I \times t$. Energy efficiency could be calculated on the $\eta = W_{H2}/W_E = (n \times \Delta H)/(Q \times Eap)$ and the *Eap* was the external voltage; *n* was the moles of hydrogen production in the standard conditions; ΔH was the combustion heat of 1 mol of hydrogen.

3. Results and discussion

3.1. Enhanced bioelectrochemical properties of MECs by AHLs

The ability of extracellular electron transfer is one limiting step from anodic communities to solid electrode, which fundamentally

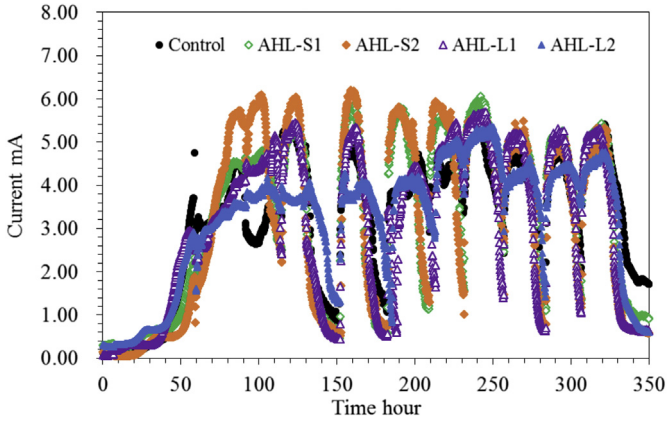

Fig. 1. Current generation of MECs after inoculation (two 24-h) with different addition of AHLs with an applied voltage of 0.8 V vs. SHE.