ARTICLE IN PRESS

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–9

Available online at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/he

Microbial electrolysis cell powered by an aluminum-air battery for hydrogen generation, in-situ coagulant production and wastewater treatment

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ARTICLE INFO

Article history:
Received 27 November 2017
Received in revised form
1 February 2018
Accepted 26 February 2018
Available online xxx

Keywords:
Microbial electrolysis cell
Aluminum-air battery
Hydrogen
Coagulation

ABSTRACT

Microbial electrolysis cells (MECs) are an efficient technology for generating hydrogen gas from organic matters, but an additional voltage is needed to overcome the thermodynamic barrier of the reaction. A combined system of MEC and the aluminum-air battery (Al-air battery) was designed for hydrogen generation, coagulant production and operated in an energy self-sufficient mode. The Al-air battery (28 mL) produced a voltage ranged from 0.58 V to 0.80 V, which powered an MEC (28 mL) to produce hydrogen. The hydrogen production rate reached 0.19 ± 0.01 m^3 $H_2/m^3/d$ and 14.5 ± 0.9 mmol H_2/g COD. The total COD removal rate was $85 \pm 1\%$, of which MEC obtained $75 \pm 1\%$ COD removal and $10 \pm 1\%$ COD removal was achieved by in-situ coagulating process. The microorganisms removal of MEC effluent was $97 \pm 2\%$ through ex-situ coagulating process. These results showed that the Al-air battery-MEC system can be operated in energy self-sufficient mode and recovered energy from wastewater with high quality effluent.

Introduction

Hydrogen is considered as a kind of clear and high efficient source of energy, which can be produced by fossil fuel pyrolysis, water electrolysis and microbial fermentation [1–4]. The pyrolysis of fossil fuel is not sustainable and release large amount of CO_2. Water electrolysis is a kind of clean technology, yet needs more energy [5,6]. The limitation of microbial fermentation to produce hydrogen is that the fermentation process is an incomplete oxidation process, the majority of the electrons can't be used to produce hydrogen and thus

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https://doi.org/10.1016/j.ijhydene.2018.02.170

induce lower substrates recovery rate [7–9]. Microbial electrolysis cell (MEC) is a bioelectrochemical system that exoelectrogens on the anode produce electrons and protons using organic chemicals, hydrogen was generated on cathode by the reduction of protons [10,11]. Recently studies showed that many alternative power sources can replace direct current power to enhance the economic benefit of hydrogen production in MEC [5,12–16]. However, MEC is still energy-intensive to produce hydrogen as MEC need external voltage (0.20 V - 0.8 V in practice) [7].

Combined MFC and MEC systems were reported as the system can obtain hydrogen harvest from wastewater without extra electricity [13,14]. Single MFC output voltage is insufficient for hydrogen generation, so multiple MFCs and capacitors were used to improve the extra voltage of MEC and the hydrogen production rate reached 0.72 m^3 $H_2/m^3/d$ [15]. Dye sensitized solar cell as a power supply to MEC was studied to use solar energy, a maximum hydrogen production rate reached 0.5 m^3 $H_2/m^3/d$ [17], but the system can't work without light. The combination of MEC with other treating processes were also studied for waste disposal to produce hydrogen. The dark fermentation effluent as MEC substrate improved the hydrogen production rate [9,18,19]. Dark fermentation and biocatalyzed MEC treating cheese whey obtained a maximum hydrogen yield of 94.2 L/H_2/kg [20]. Combined dark fermentation and dual MFCs-MEC were operated with cellulose, the hydrogen production rate achieved was 0.48 m^3 $H_2/m^3/d$ [11]. Anaerobic baffled reactor and microbial electrolysis cell operated as a two stage process can achieve higher hydrogen production and organic matter degradation [21]. Anaerobic digestion with a MEC in the digester was performed to treat food waste [22]. The combination process may be good comprehensive approach to treat complex wastewater.

When MEC is used as a technology for wastewater treatment and hydrogen production simultaneously, the MEC effluent still contains relative high COD when treating practical wastewater and need further treatment [23–25]. Coagulation process is a widely used method to treat complex wastewaters, it is also an advanced treatment method to remove low strength pollutants to improve the effluent [26,27]. Electrocoagulation (EC) is an electrochemical process producing metal ions (such as Al and Fe) and hydrolyze with water to form coagulant [28]. EC can be used for both organic and inorganic wastewaters, partial COD and nutrients can be removed from some industrial wastewater [29]. However, energy consumption is also the limiting factor for electrocoagulation technology [30,31].

Al-air battery is considered as a promising energy device as aluminum is a material with high energy density and capacity [32]. The battery comprises of three main components: aluminum anode, air cathode and electrolyte [33,34]. The reaction with neutral electrolytes in the battery were shown in equations (1)–(3). The battery anode reaction is similar with aluminum anode of electrocoagulation. Al-air battery can be a feasible structure for electrocoagulation or coagulants producing without additional electricity power [30,35]. When the Al-air battery connects with MEC, the battery can provide electricity for hydrogen generation and coagulating process combined with MEC for the treatment wastewater to obtain better effluent.

$$\text{Anode}: \ Al \rightarrow Al_3^+ + 3_{e^-} \tag{1}$$

$$\text{Cathode}: \ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{2}$$

$$\text{Overall}: \ 4Al + 3O_2 + 6H_2O \rightarrow 4Al(OH)_3 \tag{3}$$

In this study, a combined Al-air battery-MEC system was constructed for hydrogen production and wastewater treatment. The optimal conditions of Al-air battery electrolyte concentration and pH to maximize the coagulants production with single battery were investigated. The Al-air battery-MEC system was operated for hydrogen production using synthetic wastewater with sodium acetate, the MEC effluent was further treated by coagulating process using Al-air battery. The system is promising to treat complex wastewater combined coagulation and bioeletrochemical technology without external energy input and realize resource recovery.

Materials and methods

Al-air battery-MEC system construction

The integrated system was constructed by an MEC reactor and an Al-air battery (Fig. 1). The cube-shaped single chamber MEC and Al-air battery were both prepared by plexiglass with a cylindrical chamber (4 cm in length by 3 cm in diameter, empty volume = 28 ml) [36,37]. The MEC was constructed according to previous study [11]. The anode of MEC was carbon brush which was pretreated by heating method [38]. The cathode was composed of carbon cloth (B1B30WP, 30% wetproofing, E-Tek Division[SM]) coated on one side with platinum catalyst (0.5 mg/cm^2 Pt) [39]. For the Al-air battery, the sacrificial electrode is aluminum mesh wrapped on a titanium wire, the size of the mesh is 1.5 cm × 6 cm (mesh size 20 per 1.82 cm, wire diameter = 0.40 mm). The electrode spacing distance was set at 3 cm. The cathode was prepared by rolling-press process with activated carbon, stainless steel and PTFE [40].

Al-air battery-MEC system operation

The Al-air batteries were experimented using a single battery with a 10 Ω resistor. Sodium chloride was used as Al-air battery electrolyte, with varied concentration 0–35 g/L. To evaluate the effect of pH, the pH was changed from 5.0 to 10.0 (using HCl and NaOH). To evaluate the impact of electrolyte conditions on coagulant formation in Al-air battery, the Al species of the coagulants were monitored for continuously 6 h.

The enrichment step for MEC anode was performed as previously described in MFC reactors [41]. The MFCs were inoculated with domestic wastewater (20%, v/v) from the municipal pipe network (Harbin, China) and 80% medium including 1.0 g/L sodium acetate, 50 mM phosphate buffer solution (KCl, 0.13 g/L; $NaH_2PO_4 \cdot 2H_2O$, 3.32 g/L, $Na_2HPO_4 \cdot 12H_2O$, 10.32 g/L, NH_4Cl, 0.31 g/L), vitamins 5 mL/L and minerals 12.5 mL/L [42]. After cultivating for one month, the