Desalination 365 (2015) 92–98

Contents lists available at ScienceDirect

Desalination

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

Nutrient removal and electricity production from wastewater using microbial fuel cell technique

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HIGHLIGHTS

- Removal mechanisms of phosphorus and nitrogen in two MFC systems were different.
- Phosphorus was effectively removed in two MFC systems.
- More nitrogen was removed in a single-chamber MFC than a two-chamber MFC.
- Struvite was obtained in a single-chamber MFC, but not in a two-chamber MFC.
- Phosphorus was removed by the effects of precipitation and microbial absorption.

ARTICLE INFO

Article history:
Received 30 October 2014
Received in revised form 10 February 2015
Accepted 11 February 2015
Available online xxxx

Keywords:
Microbial fuel cell
Phosphorus
Nitrogen
Struvite
Precipitation

ABSTRACT

The performances of a single-chamber microbial fuel cell (MFC) system and a two-chamber MFC system on synthetic wastewater treatment and electricity production were investigated. In the single-chamber MFC system, phosphorus and nitrogen were effectively removed in the anode chamber for struvite crystallization on the surface of the cathode. However, phosphorus in the two-chamber MFC system was effectively removed in the cathode chamber. Most of ammonium in the two-chamber MFC system ultimately was transformed to nitrites, but the removal rate of total nitrogen was low. Chemical precipitates formed in two brown glass bottles were both the mixture of phosphate, carbonate and hydroxyl compound. The difference of chemical oxygen demand (COD) removal between two systems was not significant, and the vast majority of COD was consumed by microbes in anode chambers. The performances of the two-chamber MFC and the single-chamber MFC on electricity generation vary greatly for configuration difference. The maximum voltages, coulombic efficiencies, and maximum power densities of the single-chamber MFC and the two-chamber MFC were 443 and 524 mV, 35% and 51%, and 560 and 528 mW/m^2, respectively. MFC is a possible approach for simultaneous nutrient removal and electricity production from wastewater.

1. Introduction

Phosphorus and nitrogen are familiar pollutants in domestic wastewater and animal farm wastewater, leading to eutrophication of water and deterioration of water quality [1]. Moreover, phosphorus is a limited resource, and it's one of the essential elements for all forms of life growth. It has been reported that global phosphate deposits will be depleted within the next 50 years [2]. To date, there are no alternatives for phosphorus, and its depletion may lead to a decrease in food supply. Therefore, looking for renewable methods for phosphorus recovery from wastewater has become an important issue worldwide.

Magnesium ammonium phosphate (MAP, $MgNH_4PO_4 \cdot 6H_2O$, also known as struvite) is known to be an excellent slow-release fertilizer, which has been widely used in soils with a relatively low pH. MAP crystallization is a promising method for simultaneous recovery of phosphorus and nitrogen from wastewater through the following chemical reaction [3]:

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O\downarrow.$$

Struvite crystallization occurs under alkaline conditions for the solubility of struvite decreases with increasing pH, and the effective struvite

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http://dx.doi.org/10.1016/j.desal.2015.02.021
0011-9164/

crystallization has been observed at pH > 8 [4]. Struvite precipitation is affected by a number of factors, in which pH is the most important one. Most research on struvite recovery has focused on increasing solution pH via chemical base addition (NaOH, $Ca(OH)_2$, $Mg(OH)_2$). While this approach is effective, operational costs associated with chemical base addition are high accounting for up to 97% of struvite crystallization costs [5].

Recently, microbial fuel cells (MFCs) have attracted much attention as a new technology for simultaneous wastewater treatment and electricity production [3,6,7]. MFCs convert the energy stored in chemical bonds in organic compounds to electrical energy through the catalytic reactions by microorganisms.

Struvite crystals were obtained on the surface of the liquid side of the cathodes of some single-chamber MFCs [8,9] and microbial electrolysis cells (MECs) [10]. The pH near the cathode was found higher than the other site in the cathode chamber. This finding is consistent with the fact that there is a local pH increase near the cathode [11], where water is being consumed and hydroxide is generated as a byproduct [12]. Furthermore, due to cation transportation from the anode chamber to the cathode chamber across the proton exchange membrane (PEM) and the consumption of protons in the oxygen reduction reaction, pH in the cathode chamber increases significantly. It has been reported that the pH of the catholyte can reach 12 [13]. However, to the best of our knowledge, no struvite crystal was obtained in two-chamber MFCs, even though the reactor had good removal effect on nitrogen and phosphorus. The results illustrated above lead us to suspect that the mechanisms of phosphorus and nitrogen removal in the single-chamber MFC and the two-chamber MFC may be different.

To meet the requirements for different wastewater treatments using MFC technology, we must choose the most appropriate configuration. Therefore, we have to figure out the removal mechanism and removal efficiency of nutrient in MFCs with different configurations. Typical configurations of MFC are the single-chamber MFC and the two-chamber MFC. In this research, a single-chamber MFC system and a two-chamber MFC system were used for simultaneous nutrient removal and electricity production from a synthetic wastewater. Phosphorus, nitrogen and carbon removal rates along with electricity generation were evaluated. Furthermore, the changes of the concentrations of phosphorus, ammonium, nitrite, and nitrate with operation time were recorded. Sediments deposited on the electrodes and in brown glass bottles were characterized by scanning electron microscopy (SEM). Chemical precipitates obtained were analyzed by energy dispersive spectroscopy (EDS). The objectives of this study were therefore to show that MFC with different configurations may have good effect on nutrient removal, but the removal mechanisms and efficiencies were diverse.

2. Methods

2.1. MFC configuration and operation

Two MFC systems were used: a single-chamber MFC system and a two-chamber MFC system. The single-chamber MFC system consisted of a single-chamber MFC and a brown glass bottle. The brown glass bottle was independent of the single-chamber MFC. The single-chamber MFC consisted of a 4 cm long by 3 cm diameter cylindrical chamber formed from a solid block of Plexiglas plastic, as described by Call and Logan [14]. The anode was a plain carbon paper with 4 cm^2 (2.0 × 2.0 cm) projected area. The cathode (3.8 cm diameter, projected area was ~7 cm^2) was made of carbon cloth (30% wet proofed) containing a platinum catalyst (0.5 mg Pt/cm^2; liquid side), with four PTFE diffusion layers and one carbon base layer (air side). The single-chamber MFC lacked a membrane separator, and the distance between the anode and the cathode was 1.5 cm. The two-chamber MFC system consisted of a two-chamber MFC and a brown glass bottle. In addition, the brown glass bottle was connected with the cathode chamber. The two-chamber MFC was constructed based on the tubular-reactor design of Liu and Logan [15]. It consisted of two 4-cm-long cylindrical chambers (3-cm diameter, formed of Plexiglas plastic) which were separated by a PEM (3.8 cm diameter, projected area was ~7 cm^2, Nafion 117). The anode (3.8 cm diameter, projected area was ~7 cm^2, carbon paper) and the cathode (3.8 cm diameter, projected area was ~7 cm^2, carbon cloth, containing 0.5 mg Pt/cm^2) were placed on opposite sides of the PEM. The anode, PEM, and the cathode were close to each other. The catholyte was kept in a 100-mL brown glass bottle and continuously recirculated into the cathode chamber using a peristaltic pump at a flow rate of approximately 20 mL/min, as previously described by Ichihashi and Hirooka [8]. Oxygenation of solution in two brown glass bottles was supplied by air pumps, and the airflow was adjusted with air flow rotameters. The anode and cathode of MFC were connected through an external resistor with resistance of 1000 Ω (Fig. 1).

The anode and cathode chambers were inoculated with mixed anaerobic sludge and aerobic sludge (v/v = 1:1) from domestic wastewater treatment. The sludge was collected from Shijing Municipal Wastewater Treatment Plant, Guangzhou, China. Two MFCs were operated in fed-batch mode with synthetic wastewater at room temperature (25 °C–32 °C). The synthetic wastewater mainly contains $NaHCO_3$ 5.96 g/L, $NaC_2H_3O_2$ 1.00 g/L, KH_2PO_4 0.54 g/L, NH_4Cl 0.21 g/L, metals, trace minerals and vitamins. The initial pH of the synthetic wastewater was 7.00 ± 0.12. Synthetic wastewater was pumped into the anode chamber every time when the voltage decreased below 50 mV during the stable voltage output stage. The effluent from the anode chamber was subsequently directed into a 100-mL brown glass bottle. Dissolved oxygens (DOs) of anolyte in the single-chamber MFC and the two-chamber MFC were controlled at 0.02 ± 0.01 and 0.03 ± 0.01 mg/L, respectively. Meanwhile, the DOs of solution in two brown glass bottles were both controlled at 3.51 ± 0.10 mg/L throughout the study.

2.2. Analytical techniques

After MFCs achieved 3 cycles of stable voltage outputs, experiments for each treatment were carried out in duplicate. Liquid samples from the anode chamber and the cathode chamber were taken at the end of an electricity production cycle. Liquid samples were centrifuged at 8000 rpm for 5 min and the supernatants were used for measurement. Chemical oxygen demand (COD), ammonium ($N–NH_4^+$), nitrates ($N–NO_3^-$), nitrites ($N–NO_2^-$) and total phosphorus (TP) concentrations were measured according to the Standard Methods (APHA) [16]. Total nitrogen (TN) was defined as the sum of $N–NH_4^+$, $N–NO_3^-$, and $N–NO_2^-$. Bulk solution pH was tested using a pH meter (PHS-25, Leici, China). DO was measured with a dissolved oxygen meter (JPB-607, Leici, China). The dried precipitates on the electrodes, in the chambers and brown glass bottles were scraped off with a plastic sheet. Precipitates obtained during the tests were washed and re-suspended in milli-Q water to remove soluble chemicals, and then they were centrifuged again at 8000 rpm for 5 min. These re-suspension and centrifugation steps were repeated twice, and finally the precipitates were dried in a dried pot. The dried precipitate samples were characterized using a scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS, Carl Zeiss EVO LS10, DE) to examine the morphology as well as elemental composition.

The cell voltage (U) across an external resistor in the MFC circuit was automatically monitored at one-minute intervals using a data logger (M2700, Keithley, USA). Current ($I = U / R$) and power ($P = IU$) were calculated using the values of U and the external resistance (R, 1000 Ω) according to Ohm's law. The areal current density and power density were obtained using $P_d = IU / A$, where A is the projected surface area of the anode. Coulombic efficiency (CE) was calculated as previously described by Chen et al. [17]. Polarization curve was detected by verifying external resistances from 30 to 50,000 Ω with an interval of every minute to gain stable voltages. The internal resistance and