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Coupling of anaerobic digester and microbial fuel cell for COD removal and ammonia recovery

Taeyoung Kim [a], Junyeong An [a], Jae Kyung Jang [b], In Seop Chang [a,*]

[a] School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 500-712, Republic of Korea
[b] Energy and Environmental Engineering Division, National Institute of Agricultural Science, Rural Development Administration, Jeonju-si 560-500, Republic of Korea

HIGHLIGHTS

- COD and TAN removal using MFC.
- AD leading to the decrease in COD/TAN ratio.
- Decreased COD removal and CH_4 production in AD due to the decreased COD/TAN ratio.
- TAN removal in MFC resulting in an increased COD/TAN ratio.
- Increased COD/TAN ratio leading to further degradation of COD.

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ABSTRACT

Microbial fuel cells (MFCs) were investigated for use in removing total ammonia nitrogen (TAN) and residual COD from effluent digested in an anaerobic digester (AD) fed with actual swine wastewater for 32 days in batch mode. Cumulative COD removal in the AD was as high as 59,647 ± 2096 mg/L (80.5% removed), whereas TAN removal in the AD was negligible at 296 ± 116 mg-N/L (5.8% removed), causing a decrease in the COD/TAN ratio from 14.5 to 3.0. In a subsequent MFC system, 77.5% of TAN was removed at 36 days, leading to an increase in COD/TAN ratio from 4.6 to 8.1. As a result, the COD in the anode was further reduced from 19,319 ± 417 mg/L to 7519 ± 554 mg/L (61.1% removed). From these results, removing the TAN in MFCs was found to increase the COD/TAN ratio, with the COD being further degraded.

1. Introduction

Anaerobic digestion (AD) is a key bioprocess in wastewater treatment processes, with the greatest benefit being its ability to bioconvert waste solids into methane gas, and has been widely used in the treatment of highly concentrated solid wastes such as livestock and poultry waste (Lo et al., 1994; Parawira et al., 2008; Sakar et al., 2009). AD is more efficient for chemical oxygen demand (COD) removal, total volatile solid destruction, and sludge reduction as compared to aerobic processes (Sakar et al., 2009). For example, the maximum COD removal rate for AD from manure has reached ~94% (Sakar et al., 2009), and theoretically 0.39 L of CH_4 (at 1 atm, 30 °C) can be obtained from the removal of 1 g COD (Raposo et al., 2011). However, despite AD processes being efficient for use in removing concentrated wastes, they have difficulty in meeting the effluent quality standards for COD (Atuanya and Aigbirior, 2002; Castrillon et al., 2002), as well as nutrients such as nitrogen and phosphorus. AD cannot be adapted to the removal of nitrogen from animal wastewater (nitrogen-rich waste) because ammonia nitrogen is only used for cell growth, i.e., there are no oxidizing agents for AD. In an anaerobic digester, no oxidizing agents (e.g., oxygen, nitrate, nitrite, and sulfate) should be added because methanogenic archaea need a redox potential between −300 mV and −330 mV in order to optimize the AD performance (Zupančič and Grilc, 2012). For this reason, most AD processes require backup processes to further remove the effluent COD and/or nutrients (Deng et al., 2006, 2008), thus increasing the operational and maintenance costs.

Recently, a new system for wastewater treatment using microbial fuel cells (MFCs) has gained attention for integration with AD, due to their utilization of effluent in electricity generation (Zhang et al., 2009) and ammonium recovery (Kuntke et al., 2012). MFCs are electrochemical bioreactors that can convert biodegradable

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* Corresponding author. Tel.: +82 62 715 3278; fax: +82 62 715 2434.
E-mail address: ischang@gist.ac.kr (I.S. Chang).

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COD (BCOD) into electricity, and consist of an anode, cathode, and separator. In the anode, electrochemically active bacteria (EAB) act as the key player to convert BCOD to electrons and form an electric field on the anode. The electrons produced by EAB are then transferred to the cathode using the potential gradient between the anode and the cathode, and are reduced using oxidants. If a cation exchange membrane is used as the separator, protons should theoretically move from the anode to the cathode. However, the real wastewater—or even synthetic wastewater—used in MFC studies contains a number of cations that compete with protons, resulting in a considerable amount of cations being transported from the anode to the cathode (Rozendal et al., 2006). With the proposed mechanism, ammonia in an MFC integrated with AD can be removed in the cathode. In addition, at a high pH over 7, a portion of NH_4^+ exists in the form of NH_3, and hence can be removed via diffusion from the anode to the cathode (Kim et al., 2008; Kuntke et al., 2012).

In existing systems, the total ammonia nitrogen (TAN) inhibits COD removal in AD; the TAN cannot be removed because AD by itself has no capability to remove it. However, if the ammonia could be controlled, it would be possible for the high COD in AD effluent to be further reduced in the MFC. To date, there is no literature that explains the mechanism for removing COD by controlling the TAN. In this work, we hypothesize that the COD/TAN ratio could be an important parameter for treating the high COD in AD effluent that contains a high concentration of TAN. For this task, we first use AD to treat swine wastewater, and then confirm that TAN inhibits COD removal. Next, we demonstrate the further removal of residual COD from the AD by controlling the TAN in an MFC. Finally, we show the importance of the COD/TAN ratio in an AD-MFC integrated system.

2. Methods

2.1. Collection and preparation of swine wastewater feedstock

Swine wastewater in this study was obtained from swine wastewater storage (Jeongeup, South Korea). The wastewater was moved to the lab and then left for 24 h as is, in order to separate the liquid and solids. After 24 h, we collected the supernatant of the sample, which was then stored in a deep-freezer (Forma Scientific, Marietta, OH, USA) at −70 °C to avoid biodegradation and changes in the wastewater properties. The swine wastewater was removed from the freezer and used as a substrate as needed. The compositions of the swine wastewater used in this study are shown in Table 1.

Table 1
Composition of swine wastewater.

Parameter	Average ± Std.	Parameter	Average ± Std.
pH	7.54 ± 0.02	Acetate (mg/L)	13,370 ± 3180
TCOD (mg/L)	73,828 ± 1804	Propionate (mg/L)	6550 ± 1390
SCOD (mg/L)	43,489 ± 1146	Butyrate (mg/L)	5610 ± 1100
T-N (mg/L)	5152 ± 266	Isobutyrate (mg/L)	2390 ± 540
TAN (mg/L)	4199 ± 27	Valerate (mg/L)	920 ± 180
SO_4^{2-} (mg/L)	421 ± 59	Isovalerate (mg/L)	2580 ± 440
T-P (mg/L)	818 ± 19	K^+ (mg/L)	3830.4 ± 30.0
TS (mg/L)	28,000 ± 3800	Na^+ (mg/L)	797.9 ± 8.1
VS (mg/L)	17,025 ± 5775	Ca^{2+} (mg/L)	244.3 ± 18.1
Alkalinity (mg/L)	14,300	Mg^{2+} (mg/L)	39.7 ± 2.0
		Al^{3+} (mg/L)	0.6 ± 0.1
		Fe^{2+} (mg/L)	6.7 ± 2.1
		Zn^{2+} (mg/L)	0.5 ± 0.0
		Cu^{2+} (mg/L)	0.3 ± 0.0
		Pb^{2+} (mg/L)	*n.d.

* Not detected.

2.2. Construction and operation of UASB system

Three identical acryl UASB reactors (inner diameter: 70 mm, height: 453 mm, working volume: 1.4 L) were constructed for anaerobic digestion from the swine wastewater. A gas–liquid–solid (GLS) separator was installed in the UASB reactors to collect the biogas; the biogas was collected in 10 L Tedlar sample bags (SKC Inc., Eighty Four, PA, USA), and counted using a commercial bubble counter (AER 208 Respirometer, Challenge Environmental Systems, Arkansas, USA) in order to calculate the gas production rate in the reactor.

Each UASB reactor was inoculated with 0.4 L of granular sludge collected from a full-scale UASB reactor (50 m^3; continuously operated for 3 years) for methane production from swine wastewater in the storage described. Thereafter, the reactors were operated in batch mode for 32 days until the CH_4 production rate becomes stable. Note that before feeding, the frozen feedstock (i.e., swine wastewater supernatant) was completely melted at room temperature (~20 °C) with no pretreatment, dilution, or pH adjustment. Liquid samples (l mL) were taken from each UASB every 2 days or 4 days for pH, COD (soluble chemical oxygen demand (SCOD), total COD (TCOD)), total nitrogen (TN), TAN, and volatile fatty acids (VFAs) analyses. Biogases (CH_4, CO_2) were detected every 1 day or 2 days (see Section 2.4 for detailed materials and methods).

2.3. MFC construction and operation conditions

Three identical air–cathode MFCs were assembled according to Kim et al. (2013). The MFCs were constructed such that four each anode and cathode electrodes (fitted to each side wall of the MFCs) were in each reactor for quick removal of organic compounds and nitrogen from the swine wastewater. The working volume of the anode in the MFCs was maintained at 320 mL. The individual MFC reactors consisted of an acrylic anode chamber (6 cm length, 6 cm width, 6 cm height), carbon felt as the anode (Electrosynthesis, Amherst, NY, USA), carbon cloth as the cathode (BIA, BASF Co. NJ, USA), and a cation exchange membrane (Nafion® NAF NR212, Dupont Co. Wilmington, DE, USA). The membrane-based anode and cathode surface areas were each equivalent to 15 cm^2. The membrane was pretreated in a manner identical to the reference (Jang et al., 2005), and the carbon cloth was coated with a Pt catalyst (0.5 mg/cm^2) (An et al., 2011). The anode chamber and the electrodes were sandwiched together with silicon gaskets to prevent anolyte leakage, and the membrane was then positioned between the electrodes. A rectangular stainless steel ring was used as the current collector (thickness: 0.2 mm) for the cathode, which was in physical contact with the platinized cathode electrode. A current collector (titanium wire: 1.0 mm diameter) for the anode was also inserted into the anode electrode. All MFCs were operated in an incubator (Hanbaekst Inc., Korea) at 30 °C throughout these experiments.

Individual anodes were inoculated with 10% swine wastewater and 10% fermented waste in a UASB for 32 days as the EAB source, and then acclimated using an external resistance of 1 kΩ under batch mode at 30 °C until confirmation of saturated current generation. During MFC operation, a substantial evaporation of the anolyte was detected, likely due to the high temperature and low humidity. Hence, before collecting liquid samples from the MFCs, we added deionized water to the anode chambers to replenish and maintain the initial working volume. Then, 1 mL liquid samples were collected from the MFCs to analyze the pH, COD (SCOD and TCOD), TN, TAN, and VFA. All experiments were conducted in triplicate (see Section 2.4 for detailed materials and methods).