

Article

Bioelectrochemical Methane Production from Food Waste in Anaerobic Digestion Using a Carbon-Modified Copper Foam Electrode

Zhengkai An ¹, Qing Feng ^{1,*}, Rusong Zhao ² and Xiaoli Wang ²

¹ College of Environmental Science and Engineering, Qilu University of Technology (Shandong Academy of Sciences); Jinan 250353, China; qgd2016azk@126.com

² Shandong Analysis and Test Centre, Qilu University of Technology (Shandong Academy of Sciences); Jinan 250353, China; zhaors1976@126.com (R.Z.); wxlatc@163.com (X.W.)

* Correspondence: qingfeng@qlu.edu.cn

Received: 29 February 2020; Accepted: 23 March 2020; Published: 1 April 2020



Abstract: Anaerobic bioelectrochemical digestion (ABD) is widely used for treating wastewater and recovering energy. The electrode is the key point for ABD system, which was sparsely studied with food waste. In this study, a carbon-modified copper foam was fabricated with copper foam and multiple wall carbon nanotubes (MWCNT) through electrophoretic deposition and screen-printing methods. The carbon-modified copper foam electrode was investigated in an ABD reactor for food waste. The features of bioelectrochemical methane production, process stability, and electrochemical characterization were evaluated in the ABD reactor, and were compared to the control reactor without equipping electrode. The ultimate methane production reached 338.1 mL CH₄/L in the ABD reactor, which was significantly higher than the 181.0 mL CH₄/L of the control reactor. The methane produced from the electrode was 137.8 mL CH₄/L, which was up to 40.8% of total methane production in the ABD reactor. It was attributed to the electroactive bacteria that were enriched and activated by the carbon-modified copper foam electrode, further activating the direct interspecies electron transfer (DIET) pathways for methane production. The cyclic voltammetry (CV) analysis showed higher redox peaks, which is one of the pieces of evidence for the enrichment of electroactive bacteria. The carbon-modified copper foam electrode has the advantages of both carbon and metal materials, and demonstrated a high possibility for use in bioelectrochemical methane production for food waste.

Keywords: carbon-modified copper foam electrode; bioelectrochemical; anaerobic digestion; food waste; methane production

1. Introduction

With the development of food processing and catering industry, the production of food waste is also rapidly increasing [1]. Food waste is characterized as having large amounts of organic matter, high moisture, high salinity, and oil, and causes serious environmental pollution without appropriate treatment [2]. At present, the main treatment methods for food waste are incineration, landfill, feed, aerobic composting, and anaerobic digestion [3]. However, these treatment methods have various limitations, such as incineration needing more heating energy due to its high moisture, and landfill causing seepage leakage and groundwater pollution [3,4]. The feed for livestock from food waste should to be disinfect with high cost, and the aerobic composting needs large area and long period, but which also causes odor and secondary pollution [2,5]. As far as anaerobic digestion technology is concerned, it is the main biological treatment for food waste, with high energy recovery efficiency while stabilizing organic matter [6,7]. However, the anaerobic digestion treatment for rapidly increasing

production of food waste is also facing bottlenecks, such as huge digestion vessels, slow organic matter removal rate, and low biogas production [8,9].

Recently, anaerobic digestion coupled with bioelectrochemical technology has significantly improved the performance of methane production and organic matter stabilization [10,11]. Anaerobic bioelectrochemical digestion can catalyze the electrochemical reaction by the electroactive bacteria adhering on the electrode, which has a wide range of applications in wastewater treatment and energy recycling fields [12,13]. The anaerobic bioelectrochemical digestion is a promising technology for renewable and sustainable production of biogases or valuable chemicals through microbially catalyzed electrolysis of organic matters with an applied voltage to maintain potential difference between the anode and cathode [11,12]. The exoelectrogenic fermentation bacteria attached on the anode decompose organic matters into protons, carbon dioxide, and electrons, and the electrons were transferred to the surface of a cathode attached with electrothrophic methanogenic archaea to immediately reduce carbon dioxide into methane [14,15]. Nowadays, some studies have reported the methane produced from electrode is only a small proportion in the anaerobic bioelectrochemical digestion, but the methane produced from the biological direct interspecies electron transfer (DIET) pathway in the bulk solution is the dominant methane production [15,16]. These reasons have led to the wide use of anaerobic bioelectrochemical digestion in the treatment of sewage sludge, food sludge, and wastewater [17].

In the bioelectrochemical system, the electrode is the key point for the treatment performance of organic matter. For the selection of electrode materials, the general consideration is biocompatibility, wide surface area, high electrical conductivity, chemical stability, mechanical strength, electrochemical catalytic activity, and cost of electrode material [11,18]. In previous studies, the metallic electrode was widely used in the bioelectrochemical systems due to its low electric resistance, easy fabrication, and shaping figuration [19,20]. However, the metallic electrode could be easily corroded due to continuous electron transfer [18,20]. Over the past few years, carbonaceous electrode, characterized as having a wide surface, high corrosion resistance, and low cost, has been preferentially used in the bioelectrochemical system [21]. Many scientists have been devoted to research on increasing the conductivity of carbonaceous electrode to improve the performance of the bioelectrochemical system [11,18]. However, the performance of carbonaceous electrode is limited, and it has difficulty in shaping figuration in the bioelectrochemical reactors [22,23]. Therefore, the performance of bioelectrochemical system could be significantly improved by exerting respective advantages of both metallic electrode and carbonaceous electrode. However, the metal and carbon combined electrode and its features of methane production have been sparsely studied in terms of anaerobic bioelectrochemical digestion for food waste.

In this study, the features of bioelectrochemical methane production was studied in anaerobic digestion of food waste by using a carbon-modified copper foam electrode. The electrode was made by adhering carbon nanotubes on the surface of copper foam using specialized methods. The performance of digester including methane production, process stability, and electrochemical characterization was investigated and compared to a control reactor without installing electrodes.

2. Materials and Methods

2.1. Electrode Preparation

Copper foam, which has the characteristics of superior mechanical strength, wide surface area, and high electrical conductivity, was selected as the basic materials of electrode with a 1.5 mm of thickness (Kunshan New Materials Co. Ltd., China). Copper foam is characterized with aperture of 0.1–10 mm (5–120 ppi), porosity of 50%–98%, permeability of 98%, and density of 0.1–0.8 g/cm³. Multiple wall carbon nanotubes (MWCNT; HQ Tec. Co. Ltd., China), a material with high bioaffinity, wide surface area, and low electric resistance, was selected for modification of copper foam. The MWCNT were soaked in the concentrated nitric acid solution to remove impurities and improve its hydrophobicity. The treated MWCNT were washed with running water until the pH exceeded 6, and were then

adhered on the surface of copper foam using an electrophoretic deposition method. An electrolyte of electrophoretic deposition was prepared with 3 g of MWCNT, 1 g of nickel dichloride, and 1 g of polyethylenimine into 1 L of deionized water [10]. The copper foam connected to the negative terminal of a direct current power supply (SS-3305D, A-BF, China) was kept into the electrolyte by using the stainless steel mesh as the counter electrode with a distance of 1 cm. The MWCNT and nickel were deposited onto the surface of copper foam by applying a voltage of 30 V for 10 mins, and then heated at 100 °C for 10 min in a drying oven [11]. Then, a MWCNT paste was screen-printed on the surface of modified copper foam for the enrichment of carbon materials and heated again. For the screen-printing method, the MWCNT paste mixed with epoxy (30% wt.) was brushed on the surface of modified copper foam through a stainless steel mesh (mesh no. 10) using a rubber brush [24]. The carbon-modified copper foam electrode was alternately treated with electrophoretic deposition and screen-printing methods three times until its surface was fully covered with MWCNT.

2.2. Reactor Start-up and Operation

A batch anaerobic bioelectrochemical digestion (ABD) reactor was made with a cylindrical plexiglass (working volume: 1 L, inner diameter: 10 cm, height: 18 cm). An airtight cap fixed with three ports for biogas sampling, biogas collecting, and reference electrode was covered on the ABD reactor (Figure 1a) [15]. The biogas sampling port and reference electrode port were sealed with butyl rubber stopper, and the biogas collecting port was connected to a water replacement gas collector using butyl rubber tube. A salt saturated solution acidified with sulphuric acid to a pH below 2 was filled in the water replacement gas collector for preventing biogas dissolution [16]. The carbon-modified copper foam electrode (length: 20 cm, width: 10 cm) was used as the anode and cathode in the ABD reactor. The assembly of anode and cathode separated with non-woven cloth was rolled into cylindrical shape with a diameter of 6 cm (Figure 1a). The anode and cathode were fixed into the ABD reactor and their potential difference was maintained at 0.3 V by connecting to the direct current power supply using a titanium wire [10]. For the operation of ABD reactor, a matured anaerobic sludge taken from a local wastewater treatment plant (Jinan, China) was sieved with a mesh sieve (mesh no. 20), and kept in a sealed containers until no biogas was generated, and then used as the inoculum. The food waste collected from a local dining hall (Jinan, China) was mashed with an electric grinder for using as the substrate. A total of 300 mL of anaerobic sludge and 700 mL of food waste was added into the ABD reactor with an organic loading rate of 2 g chemical oxygen demand (COD)/L. The characteristics of seeding sludge, food waste, and initial liquid for start-up are shown in Table 1. The ABD reactor was maintained at 35 °C in a magnetic mixing thermostat water bath (HH-2, Ruyi Co. Ltd., China), and was continuously mixed with a magnetic bar at 500 rpm. A control reactor without equipping electrode was operated under the same condition as ABD reactor for comparison (Figure 1b), and the entire experiment was repeated three times.

Table 1. Characteristics of the seeding sludge, food waste, and initial liquid of reactors.

Parameters	Seeding Sludge	Food Waste	Initial Liquid
pH	7.02	4.46	7.2
Alkalinity (mg/L as CaCO ₃)	3290	/	6000
Chemical oxygen demand (COD, mg/L)	30,725	14,382	19,200
Total solid (TS, mg/L)	26,500	15,933	16,494
Volatile solid (VS, mg/L)	12,206	10,287	11,981

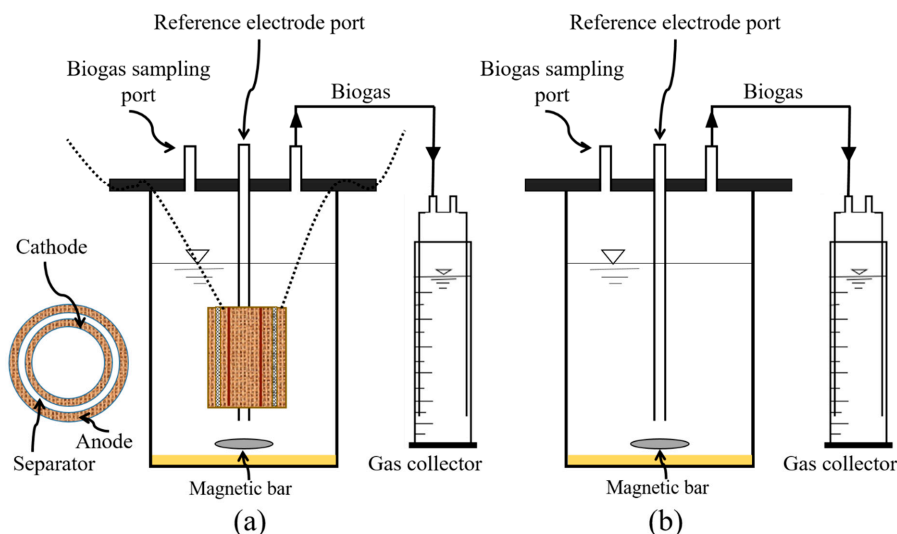


Figure 1. Schematic diagram of (a) anaerobic bioelectrochemical digestion (ABD) reactor and (b) control reactor.

2.3. Analysis and Calculation

During the operation of ABD and control reactors, the biogas composition was analyzed once a day with a gas chromatograph (SP-7990N, Ruixi Co. Ltd., China) equipped with a TDX-01 column and a fluorescence detector. The measurement of gas chromatograph and the temperatures of the injector, detector, and column were maintained at 100, 200, and 120 °C, respectively. Biogas production was monitored from the water replacement gas collector after the analysis of biogas composition. The biogas production was calibrated to the standard temperature and pressure (STP) using Equation (1) according to a previous study [16].

$$V_{CH_4}(STP, L) = \frac{273}{T + 273} \times \frac{760 - P}{760} \times V_{CH_4}(atT) \quad (1)$$

where T ($=25$ °C) is the room temperature, P (mm Hg) is the water vapor pressure at 25 °C, and V_{CH_4} (mL, at T) is the biogas volume at the room temperature. After the biogas calibration, the modified Gompertz equation was used to fit the curve of cumulative methane production (Equation (2)) [11].

$$P = P_u \exp \left[- \exp \left(\frac{\mu_m^e}{P_u} (\lambda - t) + 1 \right) \right] \quad (2)$$

where P_u (mL/L) is the ultimate methane production, μ_m (mL/L·d) is the maximum rate of methane production, and λ (day) is the lag phase time. The electric current between the anode and cathode was monitored using a digital multimeter (Keithley model 2700, Tektronic Co. Ltd., USA) in the overall experiment of ABD reactor, and the methane production via electrode was calculated from the monitored electric current with Equation (3) [24].

$$P_e(\text{mL}) = \frac{\int_0^t i dt}{Fn} \times \text{MVG} \quad (3)$$

where t (s) is the monitoring time of electric current, i (A) is the monitored electric current, F is the Faraday's constant (96,485 C/mol), n ($=8$) is the number of electrons for the methane production per mol, and MVG ($=2.24 \times 10^4$ mL/mol) is the molar volume of methane at the condition of standard temperature and pressure [24]. The behavior of the ABD and control reactors was monitored in the changes of pH, alkalinity, COD, and volatile solid (VS). The pH was monitored with a pH meter (PHSJ-3CT, Ruyi Co. Ltd, China), and the alkalinity was measured by a titration method according

to a previous study [25]. The COD and VS were measured with standard methods (2005). All data were calculated as average values and standard deviations for the three replications of the experiment. At the end of experiment, the electrochemical characteristics of bulk solution in the ABD and control reactor was analyzed by using cyclic voltammetry method. For the cyclic voltammetry of bulk solution, two pieces of stainless steel mesh (1 cm²) were immersed in the taken bulk solution for use as the working and counter electrode. The cyclic voltammetry test was analyzed in a potential range from −1 to 1 V (vs. Ag/AgCl reference electrode) with a scan rate of 1 mV s^{−1} using an electrochemical instrument (CHI800D, Chenhua Co. Ltd., China) [16]. The peak currents of cyclic voltammogram were obtained from a Smart Manager Software.

3. Results and discussion

3.1. Bioelectrochemical Methane Production

As is well known, the cumulative methane production can provide significant information for the adaptation and growth of anaerobic microorganisms. The methane production was increased rapidly after a slow increase period of 2 days in the ABD reactor (Figure 2a). The slow increase of cumulative methane production curve is the period when the bacteria are adjusting to the new environment, which is generally referred to as the lag phase [15]. As shown in Table 2, the lag phase time of ABD reactor was 2.17 days, which was calculated from the modified Gompertz equation. It indicates that the anaerobic microorganisms need approximate 2 days to adapt in the ABD reactor. However, the lag phase time was increased to 3.08 days in the control reactor. It is well known that the electroactive bacteria could be rapidly enriched on the surface of the electrode as well as the bulk solution, and further contribute to the methane production in the bioelectrochemical reactor [15,26]. The shorter lag phase time shows that the electroactive bacteria were well enriched and adapted in the ABD reactor. The methane production rate was rapidly increased after the lag phase, which could be measured and referred to as maximum methane production rate. The maximum methane production rate of ABD reactor was 90.4 mL CH₄/L.d, which was approximately two times higher than that of the control reactor (Table 2). Continuously, the ultimate methane production was accumulated to 338.1 mL CH₄/L, which was significantly higher than 181.0 mL CH₄/L of the control reactor. In conventional anaerobic digestion, methane is mainly produced through the indirect interspecies electron transfer pathway via intermediate products, such as formate, hydrogen, and acetate [24,27]. However, the bioelectrochemical methane production is attributed to the DIET pathway, which is also divided to and electrode DIET and biological DIET in the bulk solution [16,28,29]. It seems that the DIET pathways was well activated by the enrichment of electroactive bacteria in the ABD reactor. In addition, the mixing rate was considered as being slightly reduced with the presence of electrode in the ABD reactor, which could make a small error for the comparison of control reactors. However, it was believed that the activated DIET pathways were the dominant factor of influence in the ABD reactor.

Table 2. Properties of methane production and stable variables in the ABD and control reactors.

Reactors	ABD	Control
Lag phase (λ , d)	2.17 ± 0.12	3.08 ± 0.07
Maximum methane production rate (μ_m , mL CH ₄ /L.d)	90.4 ± 3.5	53.3 ± 4.3
Ultimate methane production (P_u , mL CH ₄ /L)	338.1 ± 6.6	181.0 ± 6.5
λ (d)	2.17 ± 0.12	3.08 ± 0.07
Adj-r ²	0.999	0.996
Final methane content (%)	70.2 ± 3.7	48.1 ± 2.7
Methane yield (mL CH ₄ /g COD _r)	255.3 ± 7.6	178.4 ± 6.5
Current density (A/m ²)	Total period	0.455 ± 0.011
	Stable period	0.494 ± 0.010
Methane production via electrode (mLCH ₄ /L)		137.8 ± 20.9
	pH	7.41 ± 0.02
Alkalinity (mg/L as CaCO ₃)	7405 ± 233	6015 ± 451
COD removal efficiency	65.8 ± 1.2	50.1 ± 1.5
VS removal efficiency	74.0 ± 2.2	61.3 ± 0.8

The electrode is one of the important factors of the bioelectrochemical system, and its performance is varied due to its material. In this experiment, a copper foam electrode modified by carbon material is intended to reduce corrosion and enhance its bioaffinity for electroactive bacteria. The methane production from the electrode was calculated as 137.8 mL CH_4/L , which was 40.8% of total methane production in the ABD reactor (Table 2). According to previous studies, the proportion of methane production from anaerobic bioelectrochemical digestion was in the range of 3%–30%. [16,24,28]. However, the carbon-modified copper foam electrode showed an excellent performance in this study due to its high conductivity and bioaffinity. The methane yield is the methane production from 1 g of removed COD, which represents the efficiency of energy recovery. In the ABD reactor, the methane yield was 255.3 mL $\text{CH}_4/\text{g COD}_r$ (Table 2), which was much higher than 178.4 mL $\text{CH}_4/\text{g COD}_r$ of control reactor. It indicates that the energy recovery efficiency was significantly increased due to the bioelectrochemical methane production, which is mainly attributed to the DIET pathways activated by the bioelectrochemical system [24,28]. The methane and carbon dioxide content in biogas are shown in Figure 2b. At the end of the experiment, the methane content in biogas was stabilized at 70.2%, which was much higher than 48.1% in the control reactor. In the conventional anaerobic digestion, there are four fundamental steps, including hydrolysis, acidogenesis, acetogenesis, and methanogenesis [30]. The carbon dioxide could be reduced with hydrogen via methanogens in the methanogenesis step [31]. It seems as though more carbon dioxide was converted to methane in the ABD reactor, which was further reduced carbon dioxide content in biogas. This result significantly increased the practical use of anaerobic biogas and reduced the cost of biogas purification.

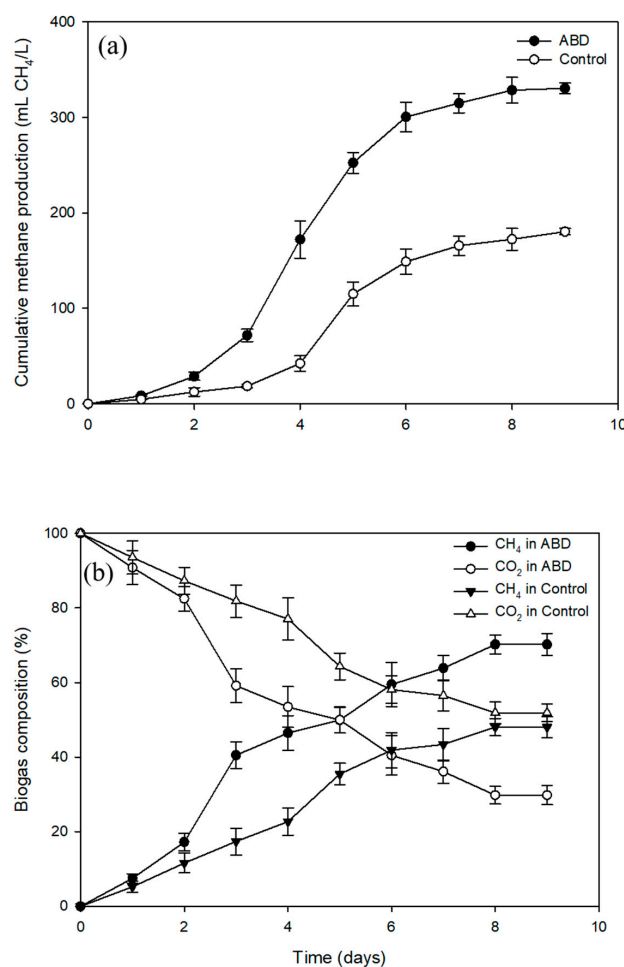


Figure 2. (a) Cumulative methane production and (b) biogas composition in the ABD and control reactors.

3.2. Process Stability

The process stability of anaerobic digestion can be evaluated from the stable variables of fermentation solution, such as pH, alkalinity, and organic matter removal. In the conventional anaerobic digestion, the favorable pH is in the range of 6.6–7.6 due to the high sensitivity of methanogens [32]. Figure 3 shows the pH changes during the operation of ABD and control reactor. The pH of fermentation solution was fixed to 7.2 with sodium bicarbonate solution at the start-up period in the ABD reactor, and slightly increased to 7.41 after a short decrease on the second day. The pH decrease was caused by the acidification of food waste in the acidogenesis step, but it turned to a self-adapted range when the acidogenesis and methanogenesis reached a balanced state [6,33]. The same phenomenon was obtained in the control reactor, wherein the pH increased from 7.2 to 7.28 (Figure 3). This indicates that the pH values of both ABD and control reactor were in the favorable range for anaerobic digestion. Generally, the pH changes are considered to be directly related to alkalinity. The alkalinity is produced by the reduction reactions of carbon dioxide to form methane, as well as sulfate reduction and decomposition of nitrogen compounds [29,34]. The alkalinity was stabilized at 7405 mg/L as CaCO₃ in the ABD reactor, which was higher than 6015 mg/L as CaCO₃ of the control reactor. It is in agreement with the higher methane production obtained in the ABD reactor, which is attributed to the DIET pathway activated by electroactive bacteria. It is well known that excessive acidification usually occurs in the anaerobic digestion of food waste, which could destroy the balance of acidogenesis and methanogenesis [7,35]. However, in the ABD reactor, both pH and alkalinity showed stronger process stability compared to the control reactor.

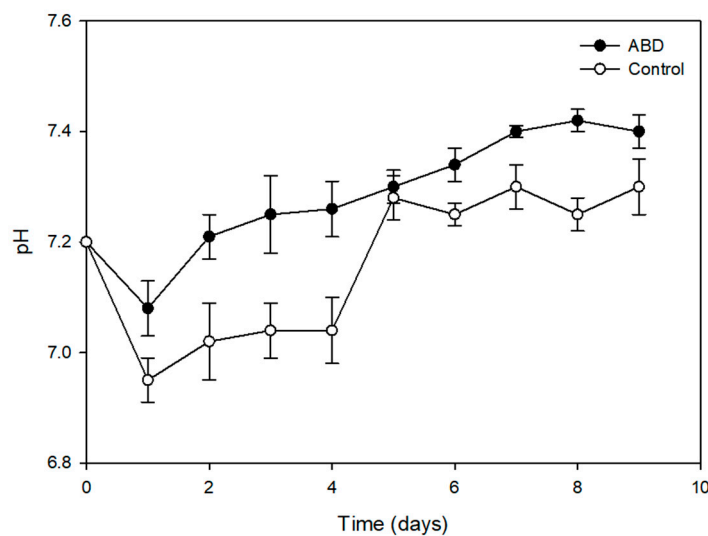


Figure 3. pH changes in the ABD and control reactors.

In the experiment of anaerobic digestion for food waste, the organic matter removal was another important indicator for evaluating process stability. The COD and VS removal efficiency were 65.8% and 74.0% in the ABD reactor, respectively (Table 2). According to previous studies, the COD removal efficiency is in the range of 30%–50%, and VS removal efficiency is in the range of 30%–60% for food waste [3,6]. It seemed as though the COD and VS removal efficiency did not reach a better value in the ABD reactor. However, in the control reactor, the COD and VS removal efficiency were reduced to 50.1% and 61.3%, respectively. This result is considered as being related to the types and composition of food waste. In this experiment, animal fat and macromolecular proteins were considered as existing in the food waste, which lead to a relative ordinary organic matter removal efficiency.

3.3. Electrochemical Characterization

The electrochemical characterization of the ABD reactor was expressed by the electrode current density and cyclic voltammetry. The current density calculated by the monitored current between anode and cathode is shown in Figure 4. At the start-up period, the current density was increased quickly at the first 2 days, and then stabilized at 0.494 A/m². It seems that the electroactive bacteria were well attached and enriched on the surface of the electrode. According to previous studies, the electroactive bacteria need approximately 10–30 days to adapt and enrich in the bioelectrochemical reactors using carbonaceous electrodes [10,29,30]. However, in this study, the carbon-modified copper foam electrode could significantly shorten the time for the enrichment of electroactive bacteria. The current density was reduced after 7 days and stabilized to 0.274 A/m² at the end of the experiment. This is in agreement with methane production due to the exhaustion of food waste.

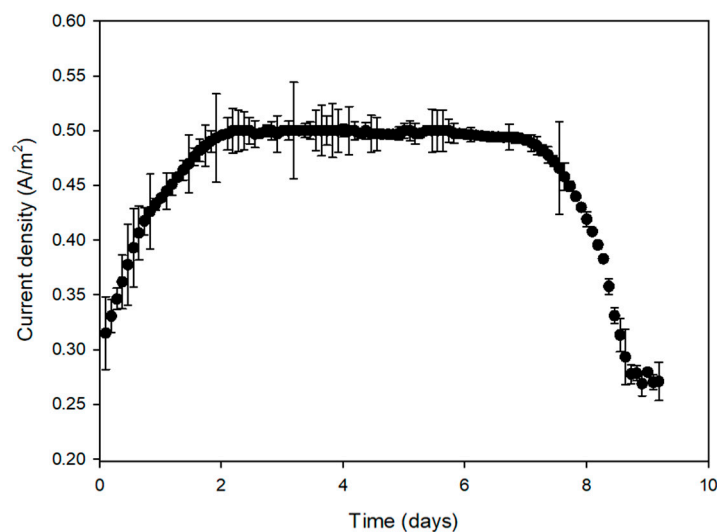
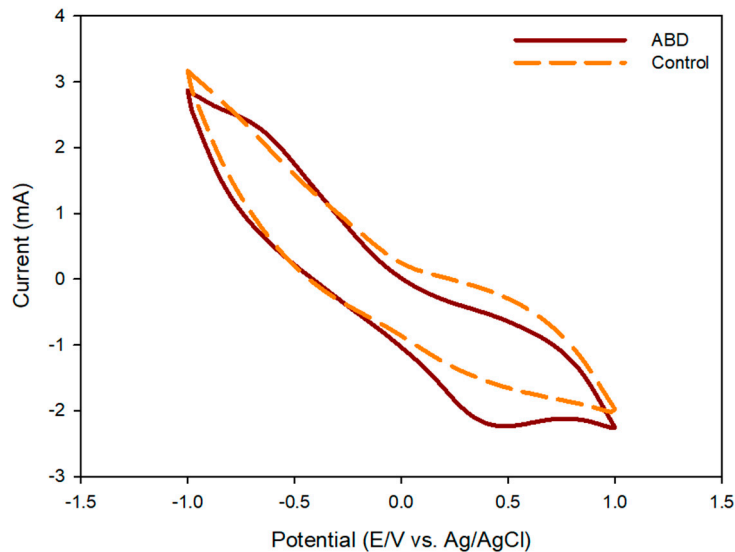


Figure 4. Changes of current density on the electrode in ABD reactor.

It is reported that the electroactive bacteria could directly transfer electrons to the extracellular electron acceptors, which widely exists in the anaerobic condition, such as in sediment [31,36]. However, the enrichment and activities of electroactive bacteria are much less without the external driving force [16,24]. The quantity of electroactive bacteria and its redox activities can be obtained from the cyclic voltammetry of bulk solution [24,37]. The cyclic voltammogram of ABD and control reactors are shown in Figure 5. In the bulk solution of ABD reactor, the oxidation peak of cyclic voltammogram is obviously higher than that of the control reactor. The oxidation current was 0.42 mA at 0.36 V (vs. Ag/AgCl) of oxidation potential (Table 3). The higher oxidation current implies the electroactive bacteria are well enriched and activated in the bioelectrochemical reactor, further facilitating the DIET pathways for methane production [38,39]. However, in the control reactor, the oxidation current was only 0.15 mA at 0.35 V (vs. Ag/AgCl) of oxidation potential (Table 3). It indicates that the common fermentation bacteria in the conventional anaerobic digestion has less oxidation activities compared to the bioelectrochemical anaerobic digestion [16]. For the reduction peak of cyclic voltammogram, the reduction current was 0.15 mA at −0.53 V (vs. Ag/AgCl) of reduction potential in the bulk solution of ABD reactor, but there was no peak obtained in that of the control reactor (Figure 5). According to previous studies, the biological DIET for methane production occurs when the electrons can be directly transferred from electroactive bacteria to methanogens [16]. It implies that there was no or very limited DIET pathway for the reduction of carbon dioxide in the conventional anaerobic digestion. These results are in agreement with features of methane production in the ABD and control reactors.

Table 3. Electrochemical parameters of cyclic voltammogram in the ABD and control reactors.

Parameters	ABD	Control
Oxidation current (mA)	0.42	0.15
Oxidation potential (V vs. Ag/AgCl)	0.36	0.35
Reduction current (mA)	0.15	Not detected
Reduction potential (V vs. Ag/AgCl)	−0.53	Not detected
Electrode current density (A/m ²)	Start-up period	0.323 ± 0.024
	Sable period	0.494 ± 0.010
	Final period	0.220 ± 0.009
		/
		/
		/

**Figure 5.** Cyclic voltammogram of bulk solution in the ABD and control reactors.

3.4. Implications

At present, the application of anaerobic digestion for food waste is more and more extensive, but there are still shortcomings such as low organic degradation, complex composition of biogas, and high risk of secondary pollution, which are not conducive to the reuse of a series of digestive products [1–4]. However, the anaerobic digestion for food waste became more stable with the equipment of the bioelectrochemical system. In the anaerobic bioelectrochemical digestion, the organic matter degradation rate was increased, and the production and content of methane were also significantly increased. These phenomena were attributed to the enrichment of electroactive bacteria, which also further activated the DIET pathways for methane production [16,28]. The electroactive bacteria are mainly enriched by the electrodes, implying the electrode is the key point for anaerobic bioelectrochemical digestion [11,18]. Generally, the carbonaceous and metallic electrodes each have advantages and disadvantages. However, in this study, we developed a carbon-modified copper foam electrode, which has higher electrical conductivity and lower corrosivity. The structure of copper foam is characterized by high porosity, high permeability, and wide specific surface area, which allows easy attachment for electroactive bacteria [11]. In addition, the strength and shaping figuration of electrodes should also be considered for the practical application. Most of the carbonaceous electrodes are breakable and attrited due to the flowing liquid in anaerobic bioelectrochemical digester [21–23]. However, the carbon-modified copper foam electrode could easily solve these problems, and is also advantageous in its fabrication, transportation, and cost. Therefore, the carbon-modified copper foam electrode is considered to have a higher performance and longer working period in the anaerobic bioelectrochemical digestion. Throughout this study, we considered and tested the comprehensive characteristics of carbon-modified copper foam electrode. It can be seen that there are many application

possibilities of the carbon-modified copper foam electrode in many different fields of bioelectrochemical systems, and it is thus worthy of further research.

4. Conclusions

The methane production from food waste was significantly increased in anaerobic bioelectrochemical digestion using a carbon-modified copper foam electrode. In the ABD reactor, the ultimate methane production was accumulated to 338.1 mL CH₄/L, which was almost two times higher than that of the control reactor. The proportion of methane production via electrode was over 40% in the ABD reactor, which was much higher than that of a carbonaceous electrode. The enrichment and activities of electroactive bacteria, as well as DIET pathways for methane production, were significantly increased in the ABD reactor. The carbon-modified copper foam electrode has the advantages of both metallic and carbonaceous electrodes, demonstrating a strong ability in the practical application of bioelectrochemical systems.

Author Contributions: Conceptualization, Q.F.; data curation, Z.A.; formal analysis, Z.A.; funding acquisition, R.Z. and X.W.; methodology, Q.F.; supervision, R.Z. and X.W.; writing—original draft, Z.A. and Q.F.; writing—review and editing, Z.A. and Q.F. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: This work was supported by the Shandong Academy of Sciences (No. 2018BSHZ0019), Jinan University and Institute Innovation Team Project (2019GXRC032) and Taishan Scholars Program (ts201712063 and ts20190948).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Lin, C.S.K.; Pfaltzgraff, L.A.; Herrero-Davila, L.; Mubofu, E.B.; Abderrahim, S.; Clark, J.H.; Koutinas, A.A.; Kopsahelis, N.; Stamatelatos, K.; Dickson, F.; et al. Food waste as a valuable resource for the production of chemicals, materials and fuels. *Energy Environ. Sci.* **2013**, *6*, 426–464. [[CrossRef](#)]
2. Girotto, F.; Alibardi, L.; Cossu, R. Food waste generation and industrial uses: A review. *Waste Manag.* **2015**, *45*, 32–41. [[CrossRef](#)]
3. Kibler, K.M.; Reinhart, D.; Hawkins, C. Food waste and the food-energy-water nexus: A review of food waste management alternatives. *Waste Manag.* **2018**, *74*, 52–62. [[CrossRef](#)] [[PubMed](#)]
4. Palmiotto, M.; Fattore, E.; Paiano, V.; Celeste, G.; Colombo, A.; Davoli, E. Influence of a municipal solid waste landfill in the surrounding environment: Toxicological risk and odor nuisance effects. *Environ. Int.* **2014**, *68*, 16–24. [[CrossRef](#)] [[PubMed](#)]
5. Li, Z.; Lu, H.; Ren, L.; He, L. Experimental and modeling approaches for food waste composting: A review. *Chemosphere* **2013**, *93*, 1247–1257. [[CrossRef](#)] [[PubMed](#)]
6. Ren, Y.; Yu, M.; Wu, C.; Wang, Q.; Gao, M.; Huang, Q.; Liu, Y. A comprehensive review on food waste anaerobic digestion: Research updates and tendencies. *Bioresour. Technol.* **2018**, *247*, 1069–1076. [[CrossRef](#)]
7. Pramanik, S.K.; Suja, F.B.; Porhemmat, M.; Pramanik, B.K. Performance and Kinetic Model of a Single-Stage Anaerobic Digestion System Operated at Different Successive Operating Stages for the Treatment of Food Waste. *Processes* **2019**, *7*, 600. [[CrossRef](#)]
8. Dhamodharan, K.; Ajay, S.K. Pre-treatment and anaerobic digestion of food waste for high rate methane production—A review. *J. Environ. Chem. Eng.* **2014**, *2*, 1821–1830.
9. Capson-Tojo, G.; Rouez, M.; Crest, M. Food waste valorization via anaerobic processes: A review. *Rev. Environ. Sci. Bio/Technol.* **2016**, *15*, 499–547. [[CrossRef](#)]
10. Feng, Q.; Song, Y.; Bae, B. Influence of applied voltage on the performance of bioelectrochemical anaerobic digestion of sewage sludge and planktonic microbial communities at ambient temperature. *Bioresour. Technol.* **2016**, *220*, 500–508. [[CrossRef](#)]
11. Feng, Q.; Song, Y.C. Surface modification of a graphite fiber fabric anode for enhanced bioelectrochemical methane production. *Energy Fuels* **2016**, *30*, 6467–6474. [[CrossRef](#)]

12. Logan, B.E.; Call, D.; Cheng, S.A.; Hamelers, H.V.M.; Sleutels, T.H.J.A.; Jeremiassen, A.W.; Rozendal, R.A. Microbial electrolysis cells for high yield hydrogen gas production from organic matter. *Environ. Sci. Technol.* **2008**, *42*, 8630–8640. [[CrossRef](#)] [[PubMed](#)]
13. Ding, A.Q.; Yang, Y.; Sun, G.D.; Wu, D.L. Impact of applied voltage on methane generation and microbial activities in an anaerobic microbial electrolysis cell (MEC). *Chem. Eng. J.* **2016**, *283*, 260–265. [[CrossRef](#)]
14. Sun, R.; Zhou, A.J.; Jia, J.N.; Liang, Q.; Liu, Q.; Xing, D.F.; Ren, N.Q. Characterization of methane production and microbial community shifts during waste activated sludge degradation in microbial electrolysis cells. *Bioresour. Technol.* **2015**, *175*, 68–74. [[CrossRef](#)] [[PubMed](#)]
15. Feng, Q.; Song, Y.C.; Ahn, Y. Electroactive microorganisms in bulk solution contribute significantly to methane production in bioelectrochemical anaerobic reactor. *Bioresour. Technol.* **2018**, *259*, 119–127. [[CrossRef](#)]
16. Feng, Q.; Song, Y.C.; Yoo, K.; Kuppanan, N.; Subudhi, S.; Lal, B. Bioelectrochemical enhancement of direct interspecies electron transfer in upflow anaerobic digester with effluent recirculation for acidic distillery wastewater. *Bioresour. Technol.* **2017**, *241*, 171–180. [[CrossRef](#)]
17. Beegle, J.R.; Abhijeet, P.B. Energy production from waste: Evaluation of anaerobic digestion and bioelectrochemical systems based on energy efficiency and economic factors. *Renew. Sustain. Energy Rev.* **2018**, *96*, 343–351. [[CrossRef](#)]
18. Feng, Q.; Song, Y.C. Decoration of graphite fiber fabric cathode with electron transfer assisting material for enhanced bioelectrochemical methane production. *J. Appl. Electrochem.* **2016**, *46*, 1211–1219. [[CrossRef](#)]
19. Guo, K.; PrevotEAU, A.; Patil, S.A. Engineering electrodes for microbial electrocatalysis. *Curr. Opin. Biotechnol.* **2015**, *33*, 149–156. [[CrossRef](#)]
20. Guo, K.; Hidalgo, D.; Tommasi, T. Pyrolytic carbon-coated stainless steel felt as a high-performance anode for bioelectrochemical systems. *Bioresour. Technol.* **2016**, *211*, 664–668. [[CrossRef](#)]
21. Mook, W.T.; Aroua, M.K.T.; Chakrabarti, M.H. A review on the effect of bio-electrodes on denitrification and organic matter removal processes in bio-electrochemical systems. *J. Ind. Eng. Chem.* **2013**, *19*, 1–13. [[CrossRef](#)]
22. Jiang, X.; Lou, S.; Chen, D.; Shen, J.; Han, W.; Sun, X.; Wang, L. Fabrication of polyaniline/graphene oxide composite for graphite felt electrode modification and its performance in the bioelectrochemical system. *J. Electroanal. Chem.* **2015**, *744*, 95–100. [[CrossRef](#)]
23. Gooding, J.J.; Gonçalves, V.R. Recent advances in the molecular level modification of electrodes for bioelectrochemistry. *Curr. Opin. Electrochem.* **2017**, *5*, 203–210. [[CrossRef](#)]
24. Feng, Q.; Song, Y.C.; Yoo, K.; Kuppanan, N.; Subudhi, S.; Lal, B. Influence of neutralization in acidic distillery wastewater on direct interspecies electron transfer for methane production in an upflow anaerobic bioelectrochemical digester. *Int. J. Hydrog. Energy* **2017**, *5*, 228. [[CrossRef](#)]
25. Anderson, G.K.; Yang, G. Determination of bicarbonate and total volatile acid concentration in anaerobic digesters using a simple titration. *Water Environ Res.* **1992**, *64*, 53–59. [[CrossRef](#)]
26. Choi, K.S.; Sanath, K.; Booki, M. Bioelectrochemical methane (CH₄) production in anaerobic digestion at different supplemental voltages. *Bioresour. Technol.* **2017**, *245*, 826–832. [[CrossRef](#)]
27. Chen, S.; Zhang, J.; Wang, X. Effects of alkalinity sources on the stability of anaerobic digestion from food waste. *Waste Manag. Res.* **2015**, *33*, 1033–1040. [[CrossRef](#)]
28. Zhao, Z.Q.; Zhang, Y.B.; Wang, L.Y.; Quan, X. Potential for direct interspecies electron transfer in an electricanaerobic system to increase methane production from sludge digestion. *Sci. Rep.* **2015**, *5*, 11094. [[CrossRef](#)]
29. Song, Y.C.; Feng, Q.; Ahn, Y. Performance of the bio-electrochemical anaerobic digestion of sewage sludge at different hydraulic retention times. *Energy Fuels* **2016**, *30*, 352–359. [[CrossRef](#)]
30. Feng, Q.; Song, Y.C.; Kim, D.H.; Kim, M.S.; Kim, D.H. Influence of the temperature and hydraulic retention time in bioelectrochemical anaerobic digestion of sewage sludge. *Int. J. Hydrog. Energy* **2019**, *44*, 2170–2179. [[CrossRef](#)]
31. Rotaru, A.E.; Shrestha, P.M.; Liu, F.; Shrestha, M.; Shrestha, D.; Embree, M.; Lovley, D.R. A new model for electron flow during anaerobic digestion: Direct interspecies electron transfer to Methanosaeta for the reduction of carbon dioxide to methane. *Energy Environ. Sci.* **2014**, *7*, 408–415. [[CrossRef](#)]
32. Liu, C.F.; Yuan, X.Z.; Zeng, G.M.; Li, W.W.; Li, J. Prediction of methane yield at optimum pH for anaerobic digestion of organic fraction of municipal solid waste. *Bioresour. Technol.* **2008**, *99*, 882–888. [[CrossRef](#)] [[PubMed](#)]

33. Kang, X.R.; Liu, Y. Chemically Enhanced Primary Sludge as an Anaerobic Co-Digestion Additive for Biogas Production from Food Waste. *Processes* **2019**, *7*, 709. [[CrossRef](#)]
34. Koch, C.; Kuchenbuch, A.; Kretzschmar, J.; Wedwitschka, H.; Liebetrau, J.; Muller, S.; Harnisch, F. Coupling electric energy and biogas production in anaerobic digesters—Impacts on the microbiome. *RSC Adv.* **2015**, *5*, 31329–31340. [[CrossRef](#)]
35. Chow, W.L.; Chong, S.H.; Lim, J.W.; Chan, Y.J.; Chong, M.F.; Tiong, T.J.; Chin, J.K.; Pan, G.T. Anaerobic Co-Digestion of Wastewater Sludge: A Review of Potential Co-Substrates and Operating Factors for Improved Methane Yield. *Processes* **2020**, *8*, 39. [[CrossRef](#)]
36. Yoon, S.M.; Choi, C.H.; Kim, M.; Hyun, M.S.; Shin, S.H.; Yi, D.H.; Kim, H.J. Enrichment of electrochemically active bacteria using a three-electrode electrochemical cell. *J. Microbiol. Biotechnol.* **2007**, *17*, 110–115.
37. Baron, D.; LaBelle, E.; Coursolle, D.; Gralnick, J.A.; Bond, D.R. Electrochemical measurement of electron transfer kinetics by *Shewanella oneidensis* MR-1. *J. Biol. Chem.* **2009**, *284*, 28865–28873. [[CrossRef](#)] [[PubMed](#)]
38. Feng, Q.; Song, Y.C.; Yoo, K.; Kuppanan, N.; Subudhi, S.; Lal, B. Polarized electrode enhances biological direct interspecies electron transfer for methane production in upflow anaerobic bioelectrochemical digester. *Chemosphere* **2018**, *204*, 186–192. [[CrossRef](#)]
39. Lovley, D.R. Reach out and touch someone: Potential impact of DIET (direct interspecies energy transfer) on anaerobic biogeochemistry, bioremediation, and bioenergy. *Rev. Environ. Sci. Biotechnol.* **2011**, *10*, 101–105. [[CrossRef](#)]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).