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# Animal carcass wastewater treatment and bioelectricity generation in up-flow tubular microbial fuel cells: Effects of HRT and non-precious metallic catalyst

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## HIGHLIGHTS

- This study is the first attempt to test the feasibility of bioelectricity generation from ACW.
- MFC could harvest power from ACW simultaneously accomplish wastewater treatment.
- $MnO_2$ could serve as an alternative of catalysts for ORR in an air-cathode MFC.
- The effects of $MnO_2$ loading and HRT on MFCs performance were investigated.

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## ABSTRACT

Animal carcass wastewater (ACW) is a kind of typical high concentration organic wastewater. Up-flow tubular air cathode microbial fuel cells (MFCs) were constructed using 0, 4.0 and 8.0 mg/cm$^2$ $MnO_2$ as cathodic catalyst, respectively (MFC-0, MFC-4 and MFC-8) to test the feasibility of bioelectricity production from ACW. After a start-up period of around 55d, when hydraulic retention time (HRT) was set at 3d, MFC-4 showed best bioelectricity performance with the maximum power density of 2.19 W/m$^3$ and minimum internal resistance of 30.3 Ω, as compared to MFC-0 (1.14 W/m$^3$, 62.6 Ω) and MFC-8 (1.49 W/m$^3$, 34.5 Ω). Chemical oxygen demand (COD) and nitrate removal efficiencies of MFC-4 were 50.66% and 79.76%, respectively. Switching HRT from 3d to 6d, COD and nitrate removal efficiencies sped up while the increase rates of ammonia slowed down. The results demonstrated that ACW could be the fuel of MFCs to generate bioelectricity.



## 1. Introduction

An annual production of animal by-products and mortalities in the U.S. livestock industry is approximately 63 billion pounds (Walker et al., 2004). This number, while already considerable, continues to escalate in the event of accidental disease entry, natural disaster, or an act of terrorism. Meanwhile, the death of zoo animals, pets and wildlife may also increase the number. If not timely and appropriately disposed of, large-scale decaying carcasses would pose a great risk to human and animal health or the environment (i.e., the contamination of soil, groundwater and surface water). Nevertheless, alkaline hydrolysis has proven to be a superior alternative to incineration and burial as a method for treatment and disposal of animal carcasses, with less environment impact and lower operating costs (Sander et al., 2002). The naturally-occurring process is accelerated in the alkaline hydrolysis tissue digester, where a strong alkaline substance (sodium hydroxide or potassium hydroxide), a high temperature (150 °C, 6 h) and a high pressure (at least 4 bars) are combined to solubilize and hydrolyze animal tissues. Animal carbohydrates, lipids, proteins, nucleic acids, as well as any pathogenic microorganisms, including RNA and DNA viruses, are converted into a sterile solution composed of amino acids, small peptides, sugars, and soap, along with the minerals from the bones and teeth (Kaye et al., 1998; Thacker, 2004). Therefore, the solution, termed as animal carcass wastewater (ACW), is generated during the treatment and disposal of animal carcasses.

The ACW is a sterile, coffee-colored, alkaline solution with a soap-like odor, which contains high amounts of biochemical oxygen demand (BOD, 70 g/l), chemical oxygen demand (COD, 105 g/l), ammonia (1 g/l), organic nitrogen (8 g/l) and total phosphorus (0.4 g/l) (Das, 2008). The composition and the amount of ACW

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varied depending upon the type of carcasses, the climatic conditions, the processing conditions, and so on. ACW can only be released into a sanitary sewer in accordance with local and federal guidelines regarding temperature, pH, and BOD, which requires careful monitoring (Thacker, 2004). Meanwhile, it is also required to afford high sanitary sewer costs owing to the added BOD caused by large amounts of hydrolysate. A recent study has highlighted the possibility of using alkaline tissue digester effluent to co-compost with yard trimmings to handle the problem of over-loading limitations in some wastewater treatment plants (Das, 2008). Alternatively, the hydrolysate can be composted with biomass materials or also suitable for spray and irrigation applications as a carbon- and nitrogen-rich fertilizer. Gousterova et al. (2008) and Kalambura et al. (2008) have showed the feasibility of using hydrolysate as an eco-friendly and valuable broadacre biofertilizer with soil neutralising properties. Therefore, it is worthwhile to find a promising and sustainable approach to handle ACW safely and cost-effectively.

Microbial fuel cells (MFCs) are unique devices that convert organic and inorganic substances directly into electricity using microorganisms as biocatalysts (Logan, 2009; Lovley, 2006). Currently, various efforts are being devoted to make MFC reactor designs and materials more cost-effective and applicable. Simple reactor configurations (i.e., single-chamber MFC, stacked MFC, and upflow MFC), are developed by removing membrane and cathode chamber and using a sustainable open-air cathode (Liu and Logan, 2004; Logan et al., 2006). Cost-effective oxygen reduction reaction (ORR) catalysts (i.e., manganese dioxide, nitrogen-doped carbon nanotubes) are also applied to replace the costly platinum (Feng et al., 2011; Zhang et al., 2009). Recently, tubular MFCs have drawn increasing attentions not only due to their feasibility of scaling up (Kim et al., 2009), but also because of their improved electrochemical performance (Scott et al., 2007; You et al., 2007) and high performance for real wastewater treatment (Feng et al., 2010; Zhuang et al., 2012). For example, the tubular MFCs fed with domestic and hospital wastewaters exhibited the maximum power densities of 59 and 48 W/($m^3$ net anodic compartment (NAC)), respectively (Rabaey et al., 2005). Meanwhile, average COD removals of 0.71 ± 0.06 and 0.45 ± 0.44 kg COD/($m^3$·NAC·d) were also approached. Therefore, the tubular MFC is a kind of promising reactor for real wastewater treatment and bioelectricity generation.

Nevertheless, ACW with a high strength of COD could provide a good source of organic substances for electricity generation. To our best knowledge, the feasibility of ACW treatment and electricity generation has not been tested in the MFC. Consequently, the objectives of this study were: (i) to evaluate the feasibility of upflow tubular MFCs for simultaneous bioelectricity generation from ACW and wastewater treatment; and (ii) to study the influences of hydraulic retention time (HRT) and non-precious metallic catalyst ($MnO_2$) on performance of the MFCs.

## 2. Methods

### 2.1. Animal carcass wastewater

ACW was obtained from animal carcass digesters of a local municipal health treatment center in Guangdong, China, and stored in a refrigerator at 4 °C prior to use. The raw ACW had very high levels of COD (78.3 ± 10.5 g/l), total nitrogen (9.56 ± 0.75 g/l) as well as ammonia nitrogen (6.75 ± 0.56 g/l) and nitrate nitrogen (0.61 ± 0.05 g/l). The pH of the raw wastewater was 6.86 ± 0.13. The raw ACW was diluted seven times in consideration of the tolerant concentration of seed bacteria, the periods of organic matter consumption and ammonia inhibitory effect. The diluted ACW was served as the substrate without any modifications or nutrient additions.

### 2.2. MFC configuration and operation

An up-flow tubular air cathode MFC was constructed based on a 10 cm diameter and 18 cm high cylindrical Plexiglas tube (5 mm thick) with the total reactor volume of 1200 ml. Graphite felt (8 mm thick, 16 × 20 cm in size, Liaoyang Jingu Carbon Fiber Technology Co., Ltd, China) was nested inside the anode chamber as roll form, and functioned as the anode together with packed granular activated carbon (GAC, 300 g) with particle diameters of 2–5 mm, resulting in the NAC of 750 ml. Homemade cylindrical titanium wire mesh (2 cycles) was inserted between the packed GAC and graphite felt to collect and transfer electrons sufficiently. In order to enhance the conductivity and biocompatibility of anode materials, nitric acid-modified graphite felt with acetone-pretreated and nitric acid-modified GAC were prepared following the method described by Zhu et al. (2011). Holes (80 mm in diameter) were homogeneously perforated over the surface of the Plexiglas tube with the intervals of 80 mm, resulting in an opening area ratio of 15% available for proton transport from the anode chamber to the cathode. Cation exchange membrane (CEM, Zhejiang Chiaki sewage treatment Co., Ltd, China) was wrapped around the outer surface of the tube. Another homemade cylindrical titanium wire mesh was pressed against the membrane. Finally, the carbon fiber cloth (500 $cm^2$, T300, Toray Co., Japan), coated with four polytetrafluoroethylene (PTFE) diffusion layers on the air-facing side (Cheng et al., 2006) and a catalyst layer on the water-facing side (Zhang et al., 2009), was wrapped and attached mechanically onto the membrane using the stainless steel wires. The reactor was sealed with epoxy. The cathodes of MFCs loaded with 0, 4.0 and 8.0 mg/$cm^2$ $MnO_2$ were prepared by the same amount of mixture of graphite (2.5 mg/$cm^2$) and polyvinylidene fluoride (1.8 mg/$cm^2$) but only different amounts of $MnO_2$. The MFCs with cathodes loaded with 0, 4.0 and 8.0 mg/$cm^2$ $MnO_2$ were denoted as MFC-0, MFC-4 and MFC-8, respectively. The electrodes were connected to the external circuit by titanium wires. The schematic diagram of the up-flow tubular MFC experiment system was shown in Fig. 1.

During the initial start-up period, the reactors were inoculated with the mixture of the diluted ACW and anaerobic granular sludge supernatant (1/1, v/v). The supernatant was collected from an upflow anaerobic sludge blanket reactor fed with ACW in our laboratory. The MFC reactors were operated in batch mode until stable MFC systems were established. Afterwards, the diluted ACW was continuously pumped from feed tank into the anode chambers using peristaltic pumps (HL-2B, Shanghai jingke industrial Co., Ltd, China). The flow rates for each MFC were fixed at 10.41, 7.81, 6.25 and 5.21 ml/h to maintain HRT of 3, 4, 5 and 6 d, respectively. The overflows from the top of the reactors were collected as the effluents. The reactors were operated for at least five times of HRT at each HRT to obtain stable performances. All experiments were conducted at 30 ± 1 °C.

### 2.3. Measurements and analysis

During the whole experiments, cell voltage ($U$) across an external resistance ($R$) of 1000 Ω (unless stated otherwise) was recorded every 80 s using a digital multimeter with a data acquisition system (Model 2700, Keithley Instruments Inc., USA). Polarization and power density curves were obtained by varying the external circuit resistance over a range from 10 to 90,000 Ω when the stable voltages were achieved. Internal resistance was estimated from the linear portion of the current ($I$) versus voltage ($U$) plot according to polarization slope method (Logan et al., 2006). Current ($I = U/R$), power ($P = IU$) and Coulombic efficiency (CE) for continuous operation were calculated as previously described (Logan et al., 2006), with current and power densities normalized by the NAC.