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Can a microbial fuel cell resist the oxidation of Tomato pomace?

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HIGHLIGHTS

- First study to evaluate pomace oxidation in microbial fuel cells.
- Provided long-term impedance data (e.g. Nyquist plots) in pomace-MFCs.
- Three time-constants during the impedance analysis using mixed cultures.
- Endogenous redox-active mediators in the higher potential region (0 V Ag/Agcl).
- Influence of particulate characteristics of pomace on electrical impedance.

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ABSTRACT

The Tomato industry in the United States generates ~40 million metric tons of pomace waste on an annual basis. Here, we demonstrate the use of pomace as the feedstock for electricity production in a microbial fuel cell (MFC). The putative redox-active compounds and the particulate characteristic of the pomace influenced the temporal dynamics of polarization, impedance, and voltammetry response of pomace-MFCs (pMFC). While the open-circuit potential of pMFC was similar to its glucose-control, the polarization response of pMFC (125 W m^{-2} and 500 mA m^{-2}) was inferior to its glucose-control (290 W m^2 and 1300 mA m^{-2}), and this difference increased with increasing scales of current density and time. The pomace oxidation was associated with a redox-active mediator that undergoes a quasi-reversible reaction at higher potential (E_p = 0 V vs Ag/Agcl); its charge transfer impedance appeared as a distinct time constant in the mid-frequency region during AC electrical impedance spectroscopy analysis.

1. Introduction

The disposal rate of food scraps in the United States has reached an alarming rate of 35 million tons per year [1]. The improper disposal of food waste pose a range of environmental challenges to modern society. A ton of food waste results in nearly 0.45 tons of CO_2e emissions during its treatment and disposal process [2]. The annual CO_{2e} emission associated with the food-waste disposal have reached as high as 4 million tons. The global carbon footprint of food waste over its life cycle (3.3 Gtons of CO_2e) is greater than the total greenhouse gas emissions from countries like Russia and India. Additionally, 250 km^3 of water is being used to grow this wasted food [2].

The management of solid organic wastes (SOWs) from the processing of tomatoes (*Solanum lycopersicum*) has been a lingering enigma. Eighty five percent of the world's tomato production (~125 million tons per year) is being processed to manufacture pastes, purees, sauce, and ketchup [3]. A series of unit operations in the tomato processing plant (water flumes, washing, sorting table, pulper-refiner, and cleaning) generates significant amount of SOWs [4]. Every ton of tomato product results in 3 m^3 of wastewater (WW) due to washing, scalding, cooling, thermal treatment, and cleaning operations [5]. The state of California alone generates 5.7 billion gallons of tomato WW every year. This WW exerts high biological oxygen demand (8 lbs. BOD/ton of tomatoes) and possess high concentration of suspended solids (6 lbs. of TSS/ton) [6].

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Nearly 40% of the processed tomatoes are disposed as solid waste consisting of skin and seeds (i.e., pomace) [7]. Europe alone generates four million tons of pomace every year. The discharge of the untreated pomace results in fouling issues, disease-causing pests, and water pollution. Feeding animals with pomace may not be a legitimate solution when it contains tomatine (i.e. solanine-like alkaloid) that can be toxic to insects, dogs, and some herbivores [8,9]. A body of scientific literature suggests the possibility of recovering the by-products from the tomato processing plants [10,11].

The skin and seed in the pomace contain high nutritional value and energetic potential. The seeds possess high heating value (24.5 MJ kg^{-1}) and nearly 22.2% protein, 20.5% lipids and 157.9 μg/g of carotenoid [12,13]. The seeds are also rich in macronutrients (C, 8.5%; N, 4.9%, and H, 8.5%) and micronutrients (Cu, 17.3 mg/kg; Mn, 50% mg/Kg; Ni, 1.5 mg/kg; Na, 44.5 mg/kg, K, 5896 mg/kg) [14]. The skin is rich in amino acids (e.g. arginine) and carotenoids [4,15]. A gram of tomato cull (i.e. defective tomato) contains half a microgram of riboflavin and thiamin both of which can serve as electron-transfer mediators to promote extracellular respiratory capabilities of exoelectrogens in MFCs [16]. The pomace can also serve as a source of electron-donor in the anode of an MFC. However, there are currently no scientific studies that examined the pomace for electricity production in bioelectrochemical devices such as MFCs. Here, we present a comprehensive study that investigates the oxidation of pomace for electricity production in MFCs.

The MFCs directly convert chemical energy stored in the organic matter into electricity by the catalytic activity of microbes. An MFC does not require expensive catalysts and, instead, uses microorganisms to transform the chemical energy in the organic matter to DC electricity under ambient conditions. Some earlier MFC studies used SOWs such as food waste [17–19] and marine wastes [16,20–23]. Tomato pomace is a promising feedstock due its rich composition in sugars, vitamins, minerals, and redox-active mediators such as riboflavin and thiamin [16,22,23]. However, the particulate characteristics of the pomace can reduce its hydrolysis rates, limit the availability of soluble chemical oxygen demand in the electrolyte, and ultimately impede the electrical performance of pomace-MFCs (pMFCs).

Electrochemical impedance spectroscopy (EIS) is a useful tool that can identify and quantify the diverse sources of internal losses including charge transfer reactions (e.g. redox processes related to pomace oxidation), ohmic losses (e.g. membrane in MFCs), and diffusion limitations e.g. Refs. [24,25]. The EIS has been widely used to quantify the impedance losses in MFCs that uses monocultures or mixed microbial cultures, and pure substrates and the wastewater. To the best of our knowledge, there are no prior studies that focused on the impedance to the oxidation of the particulate organic matter in the pomace. Here, we provide a comprehensive analysis on the impedance characteristics of fed-batch pomace-MFCs (i.e. pMFCs). We will provide an evolutionary pattern of the impedance behavior in pMFCs over longer time scale (~100 days). We will identify if the electrochemical kinetics of charge transfer reactions (e.g related to redox-active intermediates from pomace oxidation, and hydrolysis of pomace) dominate ohmic losses, and the diffusion limitation to soluble chemical oxygen demand (sCOD) associated with particulate pomace. We will compare the impedance behavior of pMFCs with that using pure glucose.

2. Materials & methods

2.1. Tomato pomace and media

The tomatoes were obtained from an Immokalee, Florida farm. The tomatoes were gently washed with deionized water, cut into four quarters, placed in boiling water for 5 min, soaked in distilled water, and refrigerated at 11^{O}C for 10 min. The skin from each segment was peeled and spread on aluminum foil. The flesh (i.e. tissue, columella, pericarp, vascular bundle, and locular cavity) and the seeds were transferred to a sterile container. The seeds along with the flesh were heated at 60 °C for 18 h and subsequently cooled to room temperature. The seeds were separated from the flesh using a fine strainer and spread on aluminum foil. The separated seeds were heated at 60 °C for 45 min. The seeds were then pressed with paper towel to absorb the remaining moisture from the seeds. The pomace was obtained by mixing the dry seeds with skin (60% seeds and 40% skin on a mass basis). The pomace liquor was obtained by blending pomace with a minimal media containing following constituents: NH_4Cl, 1.24 g L^{-1}; KCl, 0.52 g L^{-1}; $NaH_2PO_4 \cdot H_2O$, 2.45 g L^{-1}; $Na_2HPO_47H_2O$, 4.576 g L^{-1}; vitamin mix, 10 ml L^{-1}; and trace minerals, 10 ml L^{-1}. The pomace liquor is used as the anolyte in a pMFC. In certain experiments, glucose (1 g L^{-1}) was mixed with minimal media to obtain glucose-supplemented minimal media (GSMM) as the anolyte in glucose-MFCs.

2.2. MFC operation

The design of the two-compartment MFC is similar to that in our earlier study (Fig. S1) [20]. The inter-electrode spacing between anode and cathode was ~5 cm, and the surface areas of the cathode and anode are 40.1 cm^2 and 30.75 cm^2 respectively. The larger cathode surface area (and ferricyanide with faster reduction kinetics and a relatively larger catholyte volume) indicates that the rate limiting steps are not related to the cathode, and instead the performance of pomace-mfc is limited by the anode surface area. An Ultrex membrane (hydrated with 5% sodium chloride at 40 °C for 24 h) was used as a separator. The pomace liquor was used as the anolyte in pMFCs. The glucose-MFC controls used GSMM as anolyte. The catholyte in this study was based on 100 mM ferricyanide and a 50 mM phosphate buffer. The inocula (source of mixed microbial population) in the anode was obtained from the primary clarifier overflow line in a wastewater treatment plant. The performance of pMFC and its glucose-control was evaluated during twelve cycles of fed-batch operation that lasted for nearly 2600 h. The spent-anolyte was removed at end of the each batch, flushed with 50 mM phosphate buffer, and the anode compartment was filled with equivalent volume of fresh pomace-liquor.

Voltage data was acquired using a DAQ/54 module (I/O Tech Inc., Cleveland OH) across an external load (RS-200, IET Labs Inc., Westbury, NY). The polarization data at each resistance was recorded by measuring the voltage value at steady state conditions. The test and control MFCs were evaluated under fed-batch mode, and analyzed with AC electrochemical impedance spectroscopy and DC cyclic voltammetry. Fig. S2 shows the photograph of the electrical configuration used to automate the data-acquisition in pMFCs. Table 1 provides the experimental details of test pMFCs and its controls, and associated information on the electrochemical techniques (e.g. polarization, impedance analysis, and cyclic voltammetry studies).

2.3. Analytical methods

5 mL samples from the anode compartment were withdrawn with a gastight syringe to measure pH using a Cole-Palmer pH electrode probe.

2.3.1. Impedance analysis

Electrochemical impedance spectroscopy (EIS) measurements were obtained with a CHI660 electrochemical workstation (CH Instruments Inc., Austin, TX). EIS measurements were also