INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–9

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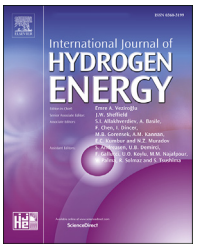

Improved process understanding and optimization by multivariate statistical analysis of Microbial Fuel Cells operation

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ARTICLE INFO

Article history:
Received 25 May 2018
Received in revised form
29 June 2018
Accepted 8 July 2018
Available online xxx

Keywords:
Bioelectrochemical systems
Principal component analysis
Wastewater treatment
Dairy wastewater
Optimization
Statistical methods

ABSTRACT

The aim of this work is to analyze Microbial Fuel Cell (MFC) processing of dairy wastewater with a multivariate statistical approach. An operating MFC was monitored for 70 days using dairy influents with varying characteristics. Results of a Principal Component Analysis (PCA) suggested that the initial dataset of 8 process-related variables could be reduced to 3 main components, explaining 80% of the cumulative variance. The first principal component (PC1) was strictly related to the conductivity of the influents and the performance of the MFC (in terms of COD removal and CE), while PC2's main contributors were: influent pH, power density and COD of the anolyte. Finally, PC3 was related to the anolyte characteristics (pH, COD_{in}) and CE. Results describe how relationships between operational variables can lead to the definition of new sets of explanatory variables to improve process visualization and to further process modifications for its optimization.

Introduction

New paradigms in wastewater treatment are currently promoting the development of process technologies beyond traditionally applied ones [1]. Renewable energiy-based processes have been proposed for the disposal of wastewaters, which consider as restrictions excessive wastefulness of energy and resources, both as energy and material, promoting their recovery [2,3]. Achieving sustainability in the waste and water treatment fields is the new frontier in environmental management [4,5]. Microbial Fuel Cells (MFCs) are considered an efficient technology, which may accomplish bioelectricity generation and wastewater depuration simultaneously [6,7]. The versatility of the process has been demonstrated by the fact that MFCs not only work well in laboratory settings with synthetic organic substrates, such as carbohydrates (i.e. glucose, acetate, fatty acids etc.) or proteins [8,9], but have also performed well in larger scale applications with complex organic matters such as domestic [10–12], livestock [13–15] and industrial wastewaters from different sources: brewery industry [16,17], dairy [18–21], food processing [22], pharmaceutical [23]. Treatment of organic fraction from municipal solid wastes [24] and landfill leachate [25–27] are also reported.

Feeding MFCs with dairy wastewater is a promising approach, considering this substrate's high organic matter content (COD > 10 g L^{-1}), biodegradability (up to 60%), and

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https://doi.org/10.1016/j.ijhydene.2018.07.056

large amounts produced (2–4 L of wastewater produced per 1 L processed milk) [28,29]. A large number of parameters and variables influence MFC's performance, since the technological aspects of the process are often complex, closely interrelated, and sometimes driven by conflicting microbiological dynamics (e.g. the competition in the anode chamber between electroactive bacteria -EABs- and methanogens). Numerous attempts to model this class of processes are ongoing, and still struggling with the intrinsic complexity of the different bioelectrochemical and microbiological aspects [30,31], associated as they may to the characteristics of the influent solution [32] feeding regime (including ionic strength, hydraulic residence time, pH, carbon source). Others are associated to the EABs metabolism or the reactors configuration, such as material and surface of electrodes, type of membrane and external resistance value [33,34]. 0-D [35], 1-D [36], 2-D [37], and 3-D models [38] for MFC have been developed; mathematical models have been also proposed for the integration of MFC with other technologies (e.g. membrane bioelectrochemical reactor, photobioelectrochemical system) [39,40]. Despite numerous efforts, bottlenecks are still present in MFC modeling: the use of simple and synthetic wastewater is not representative of more complex substrates, and a large number of models are focused on reactions happening in a single chamber (e.g. the anode), neglecting the limitations linked to the presence and importance of the other chamber (e.g. the cathode) [41,42]. In addition, more attention should be focused on the biofilm modeling, often not taken into consideration or overly simplified [30,35]. Another aspect, often underestimated, is the influence of recirculation and flow patterns on the performance and energy consumption of these systems [43–45].

Purpose of this work is to evaluate the efficiency of treatment and bioelectricity generation in an MFC fed continuously with dairy industry wastewater, while investigating the existence of potential relations between operational variables. For this, multivariate statistical analysis was applied, to investigate the feasibility of creating a dimensionally reduced model representing the process, and define a statistical framework to further optimize the operational parameters, finding better strategies to increase overall efficiency of the process. Statistical analysis has always been to the study of process models in the wastewater treatment area, generally to simplify process assessment evaluation [46–50], to simulate processes for which mechanistic modeling was not available [51,52], or to attempt process control under real-time monitoring [53–55].

Materials and methods

Design and operation of the Microbial Fuel Cell

The dual chamber MFC used in this study was built and operated as described in a previous work [56]. It consisted of two methacrylate chambers (internal volume 800 mL per chamber), i.e. anodic and cathodic chamber, both filled with 800 g granular graphite (diameter 1.5–5 mm, model 00514, EnViro cell, Germany). Granular graphite was chosen as electrode material due to its good conductivity and large specific surface for biofilm growth [57]. The presence of the granular graphite filler decreased the volume of each compartment to 435 ± 15 mL. The two chambers were separated by a cationic exchange membrane (CMI-7000, Membrane International Inc., USA), which allows the migration of cations from the anodic to the cathodic chamber. A graphite rod electrode (250 × 4 mm, Sofacel, Spain) was inserted in each chamber, as electron collector, forming an external electric circuit with a 33 Ω resistor as a load (nearly equal to the average internal resistance of the MFC, as reported in Callegari et al. [21]).

The anode and cathode were inoculated using (aerobic) activated sludge from a nearby wastewater treatment plant, as described in Molognoni et al., [56]. The anodic chamber was fed with dairy wastewater, collected from a nearby industrial cheese factory and stored at 4 °C until use. Wastewater was collected three times from the cheese factory, and, due to production variability, each collected sample had quite different characteristics, as reported in Table 1.

For this reason, three separate periods (A, B, and C) were identified. Step-feeding was adopted to maintain an average flow-rate of 1 L d^{-1}, pumping 3 L d^{-1} for 20 min per hour. The influent was stored in two collapsible 10L jerry cans, one for each solution; each change of a can corresponds to the beginning of a new cycle. A total of 15 cycles were identified; the average duration of each cycle was 4.80 ± 0.75 d. The cathodic chamber followed the same feeding routine. To develop a biocathode, trace elements and an inorganic source of carbon were added to a Phosphate Buffer Solution (PBS, 10 mM) and fed to the cathode [58]. The cathode solution contained 507 mg L^{-1} NaH_2PO_4, 819 mg L^{-1} Na_2HPO_4, 1000 mg L^{-1} $NaHCO_3$, 130 mg L^{-1} KCl, 310 mg L^{-1} NH_4Cl and other trace elements (a recipe modified from Xia et al. [58]), dissolved in tap water. To maintain a complete mixing regime, each chamber presented an internal recirculation loop of 100 L d^{-1}. An aeration basin, equipped with an air pump, was connected to the cathodic recirculation loop to obtain an oxygen-saturated catholyte. The catholyte was discharged by an overflow in the aeration basin. Anodic potentials were monitored with an Ag/AgCl reference electrode (+197 mV vs Standard Hydrogen Electrode, Xi'an Yima Opto-Electrical Technology Co., China). A data acquisition system (NI-USB 6008, National Instruments, Italy) connected to a computer was used to perform electrical measurements and control the step-feeding routine. Current and power were retrieved at 1 min intervals from MFCs voltage measurement, by application of Ohm's law. Power and current densities were evaluated dividing the respective values of power and current by the net anodic chamber volume. The experimental setup is reported in Fig. 1.

Conductivity and pH were monitored once per cycle for both anode and cathode influents and effluents (IntelliCAL™ probes + HQ40d™ Digital Meter, Hach Lange, Italy). COD of both anode influents and effluents was determined at the same interval, according to "Standard Methods" [59]. Organic Load Rate (OLR) was calculated as the daily organic matter concentration (in terms of COD) divided by the anodic Hydraulic Retention Time (HRT). Organic matter removal efficiency (η_{COD} – %) and Coulombic Efficiency (CE – %) were determined as described in Molognoni et al., [34].

Please cite this article in press as: Cecconet D, et al., Improved process understanding and optimization by multivariate statistical analysis of Microbial Fuel Cells operation, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.07.056