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Multi-system Nernst–Michaelis–Menten model applied to bioanodes formed from sewage sludge

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HIGHLIGHTS

- Efficient bioanodes were designed from hydrolyzed sewage sludge.
- Bioanodes electrochemical kinetics were studied using voltammetric analyses.
- Electrochemical systems identified displayed reversible Nernstian kinetics.
- Microbial communities were analysed by 16S-RNA pyrosequencing.

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ABSTRACT

Bioanodes were formed under constant polarization at −0.2 V/SCE from fermented sewage sludge. Current densities reached were 9.3 ± 1.2 A m^{-2} with the whole fermented sludge and 6.2 ± 0.9 A m^{-2} with the fermented sludge supernatant. The bioanode kinetics was analysed by differentiating among the contributions of the three redox systems identified by voltammetry. Each system ensured reversible Nernstian electron transfer but around a different central potential. The global overpotential required to reach the maximum current plateau was not imposed by slow electron transfer rates but was due to the potential range covered by the different redox systems. The microbial communities of the three bioanodes were analysed by 16S rRNA gene pyrosequencing. They showed a significant microbial diversity around a core of Desulfuromonadales, the proportion of which was correlated with the electrochemical performance of the bioanodes.

1. Introduction

Microbial electrochemical technologies (METs) are emergent environmentally friendly technologies that rely on electron transfer reactions catalysed by the microbial biofilms that spontaneously develop on the electrode surface. Microbial bioanodes are thus able to catalyse the oxidation of the organic matter contained in a large variety of natural environments and industrial or domestic wastes (Pant et al., 2010; Wang et al., 2012). Among these wastes, sewage sludge has been identified as a good candidate to develop and feed microbial bioanodes. Sludge is produced in large quantities all over the world as a side-product of domestic or industrial wastewater treatment. Sludge degradation requires further costly processes (Tyagi and Lo, 2013) but it could be valorized in METs, such as microbial fuel cells (MFCs), to produce electrical power.

Raw sludge, however, is mainly composed of microorganisms and consequently constitutes highly complex organic matter, which is difficult to exploit by means of MFCs (Abourached et al., 2014). Various preliminary treatments of sludge have been suggested to improve MFC performance: ultrasonication (Jiang et al., 2009; Oh et al., 2014), alkalinization (Xiao et al., 2011; Oh et al., 2014), microwave treatment or ozonation (Mohd Yusoff et al., 2013). Though a slower process, fermentation has been identified as the simplest and easiest pretreatment of sludge before it is fed into an MFC (Abourached et al., 2014; Yang et al., 2013). Fermentation does not require an external supply of energy or addition of chemicals. Moreover, more and more sewage treatment plants are being equipped with digesters, which use the raw sludge to generate methane and produce fermented sludge on site as a side-product. Fermentation results in increased volatile fatty acid (VFA) contents beneficial to the downstream MFC operation (Freguia et al., 2010; Tyagi and Lo, 2013).

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Nevertheless, the power densities and Coulombic efficiencies displayed by MFCs fed with sewage sludge still remain low (Abourached et al., 2014). Two causes can be distinguished. Firstly, the difficulties proper to the sludge itself and, secondly, the problems linked with the MFC design. As mentioned by Abourached et al. (2014), operations with sewage sludge in MFCs are hindered by non-optimized MFC designs and high internal resistance. Generally speaking, the different processes that interact in an MFC (cathode kinetics, ion migration, possible biofouling of the separator and cathode surfaces, etc.) can drastically limit the global MFC performance and lead to an underestimate of the real potential of the bioanode. The accurate characterization of the bioanode kinetics requires strict electroanalytical conditions using a three-electrode electrochemical set-up (Rimboud et al., 2014). The studies devoted to bioanodes formed in raw effluents, i.e. effluents that have not been modified or diluted by addition of buffer, salts or any other chemicals, that have been performed in electroanalytical conditions remain rare (Rimboud et al., 2014) but they have shown the great potential of the technique, for example when applied to raw effluents coming from paper mills (Ketep et al., 2013).

In this framework, the purpose of the present work was to characterize the capability of sewage sludge to form microbial anodes by breaking free of the possible detrimental interactions that occur with complete MFC devices. In this aim, bioanodes were formed under constant polarization in 3-electrode set-ups. Fermented sewage sludge was used as both the inoculum and the feeding medium for bioanode formation and operation. The bioanodes were characterized by chronoamperometry and cyclic voltammetry; their electrochemical behaviour was discussed in the light of the composition of the bacterial communities analysed by 16S rRNA gene pyrosequencing. The current densities provided by the bioanodes formed in these conditions revealed higher potential than shown so far for sewage sludge exploited in METs. The work also exposed a major drawback to be overcome for going ahead with future large-scale development.

2. Methods

2.1. Sludge collection and analysis

Activated sludge was taken from a sewage treatment plant in Evry, France. The initial pH was 6.7 and the sludge contained 41.3 g L^{-1} of solid matter. Sludge was fermented for 7 days under anaerobic conditions in a tank to favour the degradation of organic matter to volatile fatty acids (VFAs) by acidogenesis. Soluble COD increased from 288 to 1212 mg L^{-1} during this anaerobic step and the resulting fermented sludge had a pH of 7. The fermented sludge was divided into different samples which were frozen for storage. Samples were subsequently defrosted for electrochemical experiments and sludge analyses. Depending on the chosen experimental conditions, electrochemical experiments were performed on the whole sludge or on the sludge supernatant only. The sludge supernatant was obtained by 30 min centrifugation at 4000 rpm. VFA concentrations were measured in the supernatant using ion chromatography (DIONEX DX 120, column IONPAC® ICE-AS1 (9 × 250 mm)). The mobile phases were heptafluorobutyric acid (0.4 mmol L^{-1}) and TBAOH (5 mmol L^{-1}). Acetic, propionic, butyric, lactic, formic and valeric acids were found to be present in quantities ranging from 10 mg/L to 500 mg/L.

2.2. Electrochemical set-up

Bioanodes were formed and operated in 3-electrode set-ups consisting of two H-shaped compartments separated by an anion exchange membrane (Fumasep® FAA-PK, Germany) having a surface area of 7.1 cm^2. The working electrode was a 2 cm^2 carbon cloth (Paxitech®, France) connected by a platinum wire as the current collector, the counter-electrode was a 10 cm^2 platinum grid and the reference electrode was a saturated calomel electrode (SCE, potential 0.24 V vs. SHE). The working and reference electrodes were in the anodic compartment while the counter-electrode was in the cathodic compartment (see scheme in Rimboud et al., 2015). The anodic medium was 500 mL of fermented sludge of pH 8.3 after defrosting, without any addition of buffer, salts or other compound. The catholyte was a K_2HPO_4 250 mM solution, with pH adjusted to 8.3 by addition of HCl 37% in order to have the same pH in both compartments at the start of experiments. The pH was regularly measured in each compartment throughout the experiments but not controlled; it remained free to drift over time. Anodic pH remained restricted to values compatible with biofilm well-being, varying between 7.3 ± 0.2 and 8.8 ± 0.5 depending on the experimental conditions (medium renewal, acetate pulses). Cathodic pH showed higher variations, from 8.3 to 10.4 ± 0.7. The concentration of acetate was determined by means of an enzymatic measurement kit (K-acetak, Libios, France).

2.3. Procedure for bioanode formation and operation

The microbial anodes were formed under constant polarization at −0.2 V/SCE using a multichannel potentiostat (Biologic, France, EC-Lab software). Currents were recorded versus time and current densities J were expressed with respect to the geometric surface area of the anode carbon cloth (2 cm^2). At some times, the constant polarization was interrupted and cyclic voltammetry was recorded, starting from the polarization potential and scanning to −0.6 V and then back to +0.3 V/SCE at 1 mV s^{-1}. Two voltammograms were recorded in succession each time. They were mostly identical and only the second one is reported here for the sake of simplicity.

The bioanodes were first formed in a first batch (cycle 1) using 500 mL of whole fermented sludge in the anodic compartment. When the current fell down to zero, the bioanodes were removed and placed in a new reactor containing fresh sludge supernatant. Two successive batches were run in sludge supernatant (cycles 2 and 3). Each batch was considered ended when the current fell down to zero. Finally, three more cycles (cycles 4–6) were performed with pulses of 15 mM acetate (2 mL of acetate 4 M). No medium change was made during these last three cycles operated with acetate. The acetate concentration of 15 mM was chosen so as to have the same quantity of extractable electrons as with the sludge supernatant. All the electrochemical experiments were conducted in a stove thermostated at 40 °C.

The quantity of electrons extractable per litre from each VFA ([e], mol e^- L^{-1}) was calculated as the product of the VFA concentration by the number of electrons (n_e) produced by the complete oxidation of the VFA to CO_2 and protons. The quantities derived for each acid were added to estimate the quantity of electrons extractable per litre of medium.

Coulombic efficiency is defined as the ratio of the quantity of electrons effectively extracted to the quantity that could theoretically be released by complete oxidation of the substrate. For each cycle of substrate consumption, the quantity of electron extracted was determined by integrating the current with respect to time. The theoretical extractable quantity was calculated from the soluble COD of the fermented sludge (on average 1212 mg L^{-1}, 74 mmol of electrons) for the first three cycles, and from the acetate concentration (15 mM, 60 mmol of electrons) for the last three cycles.