



Experimental and theoretical characterization of microbial bioanodes formed in pulp and paper mill effluent in electrochemically controlled conditions



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HIGHLIGHTS

- Microbial bioanodes were formed in raw pulp and paper mill effluent.
- In well-controlled conditions 4 A/m^2 were reached at -0.3 V/ECS .
- A theoretical model determined the contribution of the bioanode to the COD removal.
- Electrochemical COD removal was proportional to HRT.
- Electrochemical COD removal obeyed a Michaelis–Menten law with the COD outlet.

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ABSTRACT

Microbial bioanodes were formed in pulp and paper effluent on graphite plate electrodes under constant polarization at -0.3 V/SCE , without any addition of nutriment or substrate. The bioanodes were characterized in 3-electrode set-ups, in continuous mode, with hydraulic retention times from 6 to 48 h and inlet COD from 500 to 5200 mg/L. Current densities around 4 A/m^2 were obtained and voltammetry curves indicated that 6 A/m^2 could be reached at $+0.1 \text{ V/SCE}$. A theoretical model was designed, which allowed the effects of HRT and COD to be distinguished in the complex experimental data obtained with concomitant variations of the two parameters. COD removal due to the electrochemical process was proportional to the hydraulic retention time and obeyed a Michaelis–Menten law with respect to the COD of the outlet flow, with a Michaelis constant K_{COD} of 400 mg/L. An inhibition effect occurred above inlet COD of around 3000 mg/L.

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1. Introduction

The treatment of urban and industrial effluents is a major concern of modern society and is responsible for the consumption of large amounts of energy in developed countries. Various technologies are implemented, which generally require high electricity input, particularly for the aeration of the large tanks used in aerobic treatments (Youngho and Logan, 2010), and result in the production of substantial amounts of sludge (Li et al., 2007; Stephenson et al., 2012). In recent years, an increasing number of studies have aimed to adapt the emergent technology of microbial fuel cells (MFCs) to the treatment of effluents. MFCs would offer the great advantage of abating organic matter in anaerobic conditions, thus saving the cost of aeration. In addition, they could transform a part of the chemical energy contained in the organic matter directly into electricity (Logan and Rabaey, 2012).

Paper-making is a water-intensive industrial sector that requires high volumes of water and produces high volumes of concentrated effluents. Nevertheless, few MFC studies have addressed paper mill effluents so far and they have shown only very modest performance in current and power generation (see Table 1 in Supplementary data). Abatements of the effluents' chemical oxygen demand (COD) generally seem satisfactory, but the low values of Coulombic efficiencies (CE) indicate that the electrochemical process makes only a minor contribution to COD removal. Under continuous flow in an air cathode MFC, Liu et al. obtained CE of 12% with the effluent from a treatment plant (Liu et al., 2004); Cheng et al. found maximal CE of 27% with domestic wastewater (Cheng et al., 2006). Several other studies using raw effluents have exhibited very low Coulombic efficiencies, between 1% and 5% (Youngho and Logan, 2010; Wen et al., 2010; Lee et al., 2010; Kassongo and Togo, 2011; Lefebvre et al., 2013). It is thus widely agreed that a substantial fraction of organic matter is oxidized in alternative ways such as aerobic respiration or anaerobic pathways due to the presence of dissolved electron acceptors (nitrate, sulphate)

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(Min et al., 2005; You et al., 2006; Lu et al., 2009). In parallel, fermentation processes cannot be ruled out and biomass growth has also been suggested to account for part of COD removal (Min and Logan, 2004; Liu et al., 2004). The formation of microbial bioanodes in raw effluents is consequently hard to investigate because of the large part of COD removal that is not related to electrochemical reactions.

The purpose of the present study was to identify the electrochemical performance that microbial bioanodes formed in pulp and paper effluents could reach, using well controlled electrochemical conditions. Most studies using raw industrial effluents have been carried out in whole MFC devices so far. MFCs are quite complex systems in which various processes occur and can interact (anode and cathode kinetics, diffusion and migration in different media including membrane, etc.) and multiply the number of possible causes of rate limitation. In contrast, in the present study, an electroanalysis cell including a 3-electrode set-up was used to rigorously control the potential of the microbial bioanode and to avoid any rate limitation not related to the bioanode kinetics. In particular, the high internal resistance of MFC due to the low conductivity of effluents was overcome by locating the reference electrode very close to the bioanode surface. A small electrode surface area (10 cm²) was used in a large volume of effluent (0.5 L) to favour a uniform current distribution and to maintain stable substrate concentration in the reactor. Furthermore, smooth graphite plate electrodes were used to avoid morphological enhancing effects. This cell design was established according to conventional electroanalytical rules in order to characterize the intrinsic bioanode behaviour in electrochemically rigorous conditions. Obviously, the same design would not be suitable for an industrial reactor, in which the electrode surface area must be as large as possible, the electrode morphology must favour local current heterogeneities and the use of a reference electrode cannot be contemplated. Similarly, nitrogen was sparged continuously in the electroanalysis cell to avoid aerobic side-oxidations, while it would not be useful at the industrial scale.

The electroanalysis cells were fed with effluents at different COD concentrations supplied in continuous mode with different hydraulic retention times (HRT). To remain as close as possible to industrial conditions, the effluent was used as collected from the treatment unit, without any input of nutrients or addition of substrate. This was an original approach with respect to current literature. Less than 30% of the studies dealing with MFCs have operated in continuous mode and most were conducted with pure substrates (Zhang et al., 2013).

A theoretical approach was also developed to extract conclusions from experimental data that varied in a complex manner due to the evolution of the raw effluent during long-lasting experiments. As far as we know, this study was the first attempt to use well-controlled electrochemical conditions when characterizing bioanodes operating in continuous mode in a raw effluent.

2. Experimental section

2.1. Effluent

Effluent from a recycled paper producing mill was collected at the outlet of the anaerobic effluent treatment step with COD ranging from 1400 to 1650 mg/L, pH of 7.15 ± 0.15 and conductivity of 3.3 ms/cm. It was stored at 4 °C until used. This effluent was used as sole inoculum and substrate source without addition of any nutrients or trace minerals. Lower COD values were obtained by diluting the raw effluent with fresh water. Higher COD values were reached by mixing effluents collected at the outlet and the inlet of the anaerobic process (inlet COD up to 5200 mg/L).

2.2. Bioanode formation and continuous reactor operation

Working electrodes were flat 2 cm × 5 cm × 0.5 cm graphite plates (Goodfellow) electrically connected via screwed titanium wires (Alfa Aesar). Current densities were calculated with respect to the 10 cm² projected surface area. Before use, the graphite electrodes were cleaned by 1 h in 1.0 M HCl, 20 min rinsing with distilled water, 1 h in 1.0 M NaOH and final thorough rinsing with distilled water. Auxiliary electrodes were 90% Platinum–10% Iridium grids (Heraeus). Potentials were controlled versus a saturated calomel electrode (SCE; potential +0.24 V/SHE; Radiometer, Copenhagen) using a multi-channel potentiostat (Bio-Logic SA). All experiments were achieved under constant applied potential (chronoamperometry, CA) at –0.3 V/SCE. The applied potential was periodically suspended to record cyclic voltammetry (CV) curves at 1 mV/s. The reactors were maintained at 25 °C in a temperature-controlled room and were continuously sparged with N₂ to maintain anaerobic conditions. Replicates were systematically performed as discussed below.

The bioanodes were firstly formed for around 1 week in batch mode, i.e. with the reactor filled with 500 mL raw effluent in the absence of any flow. The reactors were then continuously fed with the raw effluent thanks to a peristaltic pump. The flow rate was varied from of 250 to 2000 mL/day by steps of around a week each, which gave hydraulic retention time (HRT) values from 48 to 6 h, respectively. During the experiments, the tank, in which the effluent was stored, was kept at 4 °C under nitrogen.

Samples were collected daily from the influents (input) and effluents (output) of the reactors to measure their COD according to the ISO 15705 standard micro-method using Merck reagents and a WTW Photolab® 6000 spectrophotometer.

2.3. Calculations

Only the definitions of the conventional parameters are recalled in this section. The modelling work is described in Section 3.2.1. Hydraulic retention time (HRT, s) is the ratio of the solution volume in the reactor V_s (0.5 × 10⁻³ m³) to the volumetric flow rate (\dot{V} , m³/s):

$$\text{HRT} = \frac{V_s}{\dot{V}} \quad (1)$$

The total COD removal (ΔCOD , mg/L or g/m³) was defined as the difference between the input and output COD values:

$$\Delta\text{COD} = \text{COD}_{\text{input}} - \text{COD}_{\text{output}} \quad (2)$$

and the total COD removal yield (%) was:

$$Y_{\text{COD}} = \frac{\Delta\text{COD}}{\text{COD}_{\text{input}}} \cdot 100 \quad (3)$$

The average Y_{COD} values reported in the tables and figures were calculated from 5 to 7 daily measurements of $\text{COD}_{\text{input}}$ and $\text{COD}_{\text{output}}$. Experimental errors on COD abatements were calculated as follows:

$$2 \times u_{\text{DCO}} = 2 \times \left[\frac{1}{\text{DCO}_{\text{input}}} \right] \cdot \sqrt{u_{(\text{DCO}_{\text{input}})}^2 + u_{(\text{DCO}_{\text{output}})}^2 + \frac{(\text{DCO}_{\text{input}} - \text{DCO}_{\text{output}})^2}{\text{DCO}_{\text{input}}^2} \cdot u_{(\text{DCO}_{\text{output}})}^2} \quad (4)$$

where $u = 30$ mg/L is the experimental error on each COD measurement related to the measurement kit. In all cases, experimental errors on Y_{COD} were of 5–6%. Coulombic efficiency (CE) was calculated as the charge passed through the circuit (Q), calculated by integrating the current over a given period of time, to the charge that could be produced by complete oxidation of the effluent supplied during the same period (Q_{max}):

$$\text{CE} = \frac{Q}{Q_{\text{max}}} \quad (5)$$

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