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Short communication

Two-dimensional carbon cloth and three-dimensional carbon felt perform similarly to form bioanode fed with food waste

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A B S T R A C T

Two-dimensional carbon cloth and three-dimensional carbon felt were compared for their capacity to form bioanodes for food waste treatment. Wastewater was used as the dilution medium instead of a synthetic solution to be close to industrial conditions. In both cases, microbial cells were mainly wrapped around the fibers of the electrodes. The biofilms were around 80–120 μm thick with a 39.3% microbial volume ratio on carbon cloths. On carbon felt, the biofilms showed a lower microbial volume ratio of 16.3% on the upper layers but with a penetration depth of 200–800 μm . The biofilm patterns were different but they resulted in similar current density, around 3.5 A/m^2 . When chemically rich media have to be implemented, 2D cloth offers a worthwhile solution that can equal 3D porous materials.

Keywords:

Microbial anode
Carbon felt
Biofilm structure
Porous electrode
Microbial electrochemical technology

1. Introduction

Treating the wastes produced by food industries is a necessity for environmental, safety, and economic reasons [1]. In this context, microbial electrochemical technologies (MET) may be seen as a promising way to treat food waste by converting the chemical energy they contain into electrical energy [2–4] or hydrogen. A few studies have described the formation of microbial anodes with raw food wastes in conditions close to industrial constraints [5–7]. In particular, substituting the phosphate buffer solution used in laboratory-oriented studies by wastewater, which is costless and widely available in large amounts, ensured promising current density up to 5 A/m^2 [5].

It has been widely shown that using porous 3-dimensional structures can lead to efficient bioanodes, e.g. with graphite felt [8–10], carbon foams made from the pyrolysis of natural products [11,12], stainless steel foam [13], etc., but direct comparisons of two-dimensional (2D) and three-dimensional (3D) microbial anodes in identical conditions remain very rare [14,15]. Moreover, most of the bioanodes studied so far have been implemented in synthetic media using acetate as the substrate. In some cases, the substrate is a small volume of real waste diluted in the synthetic medium. These conditions give worthwhile results that advance fundamental knowledge but would be difficult to scale-up to large-size industrial processes because of the large amount of salts that are required to prepare the dilution.

The purpose of the present study was to assess the suitability of 3D electrode versus 2D electrodes when they are formed in close-to-

industrial conditions, i.e. using food waste as the substrate and wastewater as the dilution medium [5]. No synthetic medium was used, only food waste and domestic water effluent. 2D and 3D structures were compared using cloth and felt structures both made from similar 10- μm diameter carbon fibers.

2. Materials and methods

2.1. Electrochemical setup

Working electrode of $2 \times 3 \text{ cm}^2$ geometric surface area were implemented in 600 mL three-electrode set-ups with a saturated calomel reference electrode (SCE, Radiometer Analytical, +0.24 V/SHE) and a $2 \times 3 \text{ cm}^2$ platinum grid used as the auxiliary electrode. The working electrode was either carbon cloth (0.5 mm thickness, Paxitech, Grenoble, France) or carbon felt (5 mm thickness, RVG 4000, Mersen, France). It was located at around 10 cm from the auxiliary electrode and less than 0.5 cm to the reference electrode. The working electrode was polarized at 0.15 V/SCE using a VSP potentiostat (Bio-Logic SA, EC-Lab software) and the current was recorded every 10 min. Cyclic voltammetry was recorded at 1 mV/s in the -0.6 to $+0.3$ V/SCE range. The reactors were continuously slightly stirred and maintained at $27 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ in a water bath. They were initially purged with nitrogen for 15 min to remove oxygen.

2.2. Inoculum, wastewater, and food wastes

Activated sludge was collected from a wastewater treatment plant (Castanet-Tolosan, France) with a chemical oxygen demand (COD) of

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4100 mgO₂/L. Wastewater collected from the same plant served as the medium, with a soluble COD about 390 mg/L, ammonium 48 mg/L, nitrate less than 0.5 mg/L, and sulfate 27 mg/L and pH 7.8.

Food wastes were prepared with common food components in a reproducible way as described elsewhere [5]. The final pH was 3.4 and soluble COD 42.6 gO₂/L. Fed-batches were run with successive additions of 10 mL food waste leachate into the 600 mL wastewater, resulting in 700 mg/L COD.

2.3. Bioanode formation

Bioanodes were formed in duplicate using the procedure previously described [5,16]. Primary bioanodes were formed with 3 consecutive batches that contained wastewater, 10 mL food waste leachate, and 3.3% v/v activated sludge used as the inoculum. After 3 batches (15 days), a secondary electrode was introduced into each reactor and polarized at the same potential (0.15 V/SCE). Successive batches were run with wastewater medium and food waste only, without addition of activated sludge. Finally, the primary bioanodes were removed from the reactors at the 27th day. At the end of the experiments (37 days), the secondary bioanodes were imaged by SEM and epifluorescent microscopy.

2.4. Microscopy imaging

2.4.1. Scanning electron microscopy (SEM)

Bioanodes were fixed as described elsewhere [17] and observed with a LEO 435 VP scanning electron microscope.

2.4.2. Three-dimensional epifluorescence microscopy

Biofilms were stained with acridine orange 0.01% (A6014 Sigma) for 10 min, then carefully washed and dried at ambient temperature. The samples were imaged with a Carl Zeiss Axiomager M2 microscope equipped for epifluorescence with an HBO 50 W ac mercury light source and the Zeiss 09 filter (excitor HP450–490, reflector FT 10, Barrier filter LP520). Images were acquired with a monochrome digital camera (evolution VF) along the Z-axis and processed with the Axiovision® software. The proportion of the electrode surface covered by the biofilm was assessed by gray scale level analysis. The gray intensity threshold between biofilm-covered and non-covered areas was set manually.

2.4.3. Microbial volume ratio

Each calculation was based on a stack of 30 images performed from the upper surface along the z-axis of the bioanode with a distance (δ) of 3.9 μ m between each focal plane. The local microbial volume was assessed for each image by multiplying the biofilm-covered surface area by the thickness δ . The sum of the 30 local microbial volumes divided by the total volume of the 30 layers ($30 \times \delta \times \text{image area}$) gave the so-called “microbial volume ratio.” This value indicated the volume ratio that contained intracellular or extracellular nucleic acid in the upper biofilm layer of 117 μ m thickness.

3. Results and discussion

3.1. Electrochemical characteristics

Four bioanodes were formed according to the primary/secondary protocol under applied potential of 0.15 V/SCE, two with carbon cloth and two with carbon felt. Evolutions of the current intensities were similar for both electrode kinds (Fig. 1A). The primary bioanodes started to provide current after 4 days and reached 1.8 ± 0.2 A/m² at the third batch. The secondary bioanodes gave maximum current density of 3.5 ± 0.8 A/m². Duplicates showed different performance of the primary bioanodes (Fig. 1A') but they confirmed similar trend for the secondary bioanodes. Such a difference in the primary bioanode performance was also observed with carbon cloth electrodes and was not linked to the

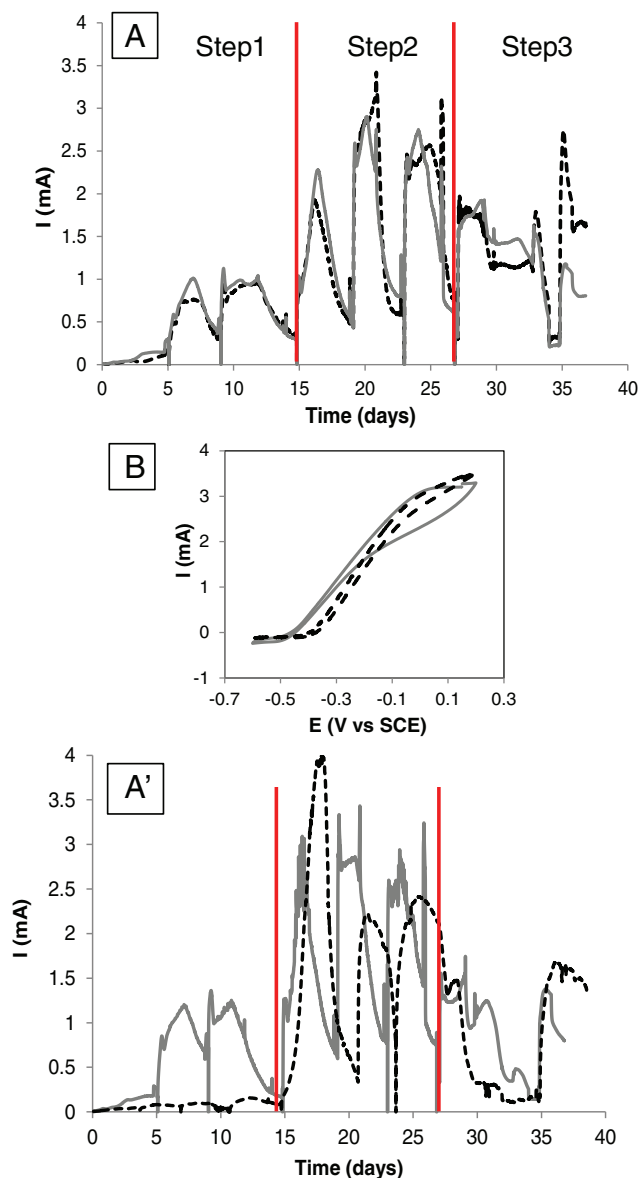


Fig. 1. Current intensity as a function of time for carbon cloth (dotted line) and carbon felt bioanodes (gray plain line) polarized at +0.15 V/SCE, fed with food waste (A and A'). The experimental conditions corresponding to steps 1–3 are described in Section 2.3. (B) Cyclic voltammeteries (1 mV/s) on the 21st day on carbon cloth (dotted line) and carbon felt bioanodes (gray plain line).

electrode material. On average, the electrocatalytic improvement from the primary to the secondary bioanode corresponded to a multiplication factor of 2, as already reported using a synthetic medium and acetate as substrate [16,18].

The turnover cyclic voltammeteries (CV) of carbon cloth and carbon felt bioanodes showed a similar sigmoidal shape with zero-current potential ranging from -0.45 to -0.40 V/SCE and an overpotential of around 0.50 V required for the maximum current be reached (Fig. 1B). The 2-dimensional carbon cloth electrodes and the 3-dimensional carbon felt electrodes led to similar electrochemical characteristics.

3.2. Electrode and biofilm imaging

SEM imaging of the clean electrodes showed that both structures were composed of the same 10 μ m diameter fibers (Fig. 2A-B). Carbon cloth had a very tight network of interwoven threads. In contrast, carbon felt presented an open structure with space between fibers ranging

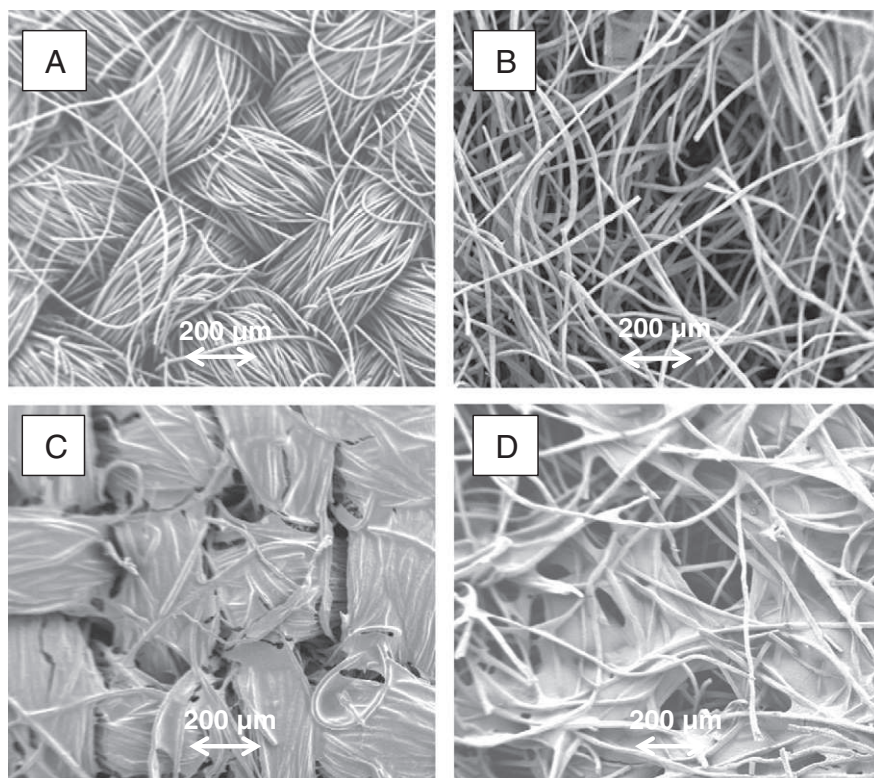


Fig. 2. SEM images of clean electrodes of A/carbon cloth, B/carbon felt, and secondary bioanodes on C/carbon cloth and D/carbon felt formed at +0.15 V/SCE (day 37).

from around 20 to 200 μm . At the end of the chronoamperometry (37 days) SEM showed an almost uniform biofilm on carbon cloth, while the carbon felt surface was only partly clogged (Fig. 2C-D).

Primary and secondary bioanodes were characterized by three-dimensional epifluorescent microscopy (Fig. 3A-B). The microbial volume ratios were $27 \pm 6.8\%$ and $12 \pm 4.4\%$ on carbon cloth and carbon felt, respectively, for the primary bioanodes. The secondary bioanodes showed a significant microbial volume increase to $39.3 \pm 1.1\%$ and $16.3 \pm 2.7\%$ on carbon cloth and carbon felt, respectively. Improvement of the current density from the primary to the secondary bioanodes corresponded to a significant microbial volume increase. The current density provided by the electrodes was straightforwardly linked to the microbial volume ratio.

Carbon cloth has a surface fully accessible for the microorganisms and led to an almost uniform biofilm with a thickness of the order of 80–120 μm and a microbial volume ratio of $39.3 \pm 1.1\%$. Carbon felt led to microbial volume ratio of only $16.3 \pm 2.7\%$. The epifluorescent

images showed that the nucleic acids were mainly accumulated around the electrode fibers (Fig. 3). The microbial volumes were consequently higher on the cloth than on the felt structure because the fibers were denser in the cloth configuration.

Sectional cuts of the carbon felt bioanodes (Fig. 4) showed that fibers on the surface are completely covered with a biofilm wrapped around them, while the fibers in the center are not colonized at all. The biofilm penetration depth measured in several spots of the sectional cut view was in the range from 200 to 800 μm . As the biofilm was settled on the two sides of the felt, which has a total thickness of 5000 μm , it can be concluded that the biofilm colonized only 8%–32% of the total felt volume.

It must be recalled that the microbial volume ratios were measured only on the 117- μm -thick upper layer of the bioanodes (see Section 2.4.3). On the felt electrode, the 117- μm upper part of the biofilm had a lower microbial volume ($16.3 \pm 2.7\%$) than the biofilm formed on the cloth ($39.3 \pm 1.1\%$) but the biofilm penetrated 200–800 μm inside

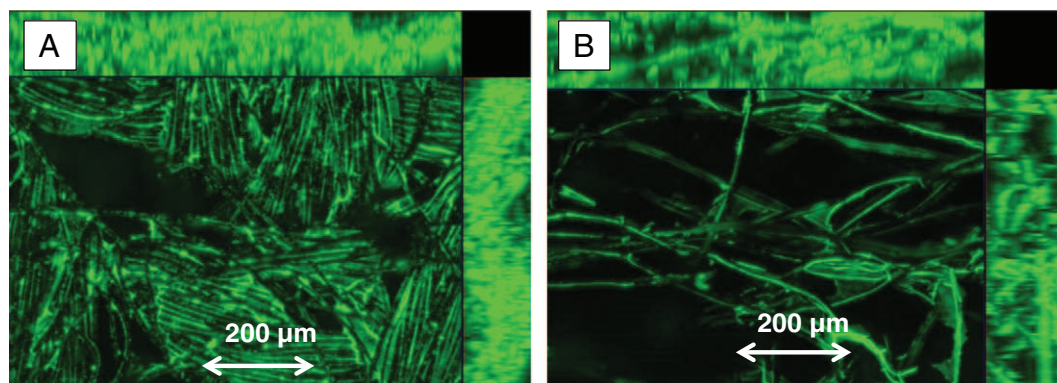


Fig. 3. 3D epifluorescent microscopy of secondary bioanodes formed under polarization at +0.15 V/SCE on A/carbon cloth and B/carbon felt (day 37).

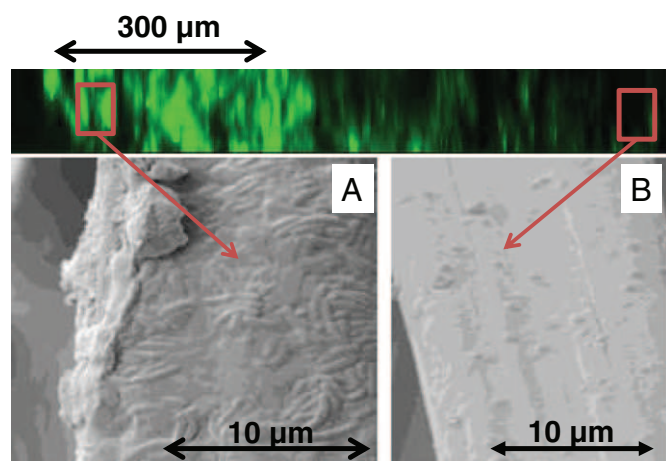


Fig. 4. Sectional views of a carbon felt secondary bioanode (37 day) observed by epifluorescent microscopy (on top) and SEM of two different fibers (A) on the surface of the carbon felt (B) 1 mm deep in the carbon felt (B).

the felt electrode. The biofilm penetration inside the felt compensated for the lower microbial volume, and resulted in similar electrochemical performance for both structures.

For both structures, SEM showed a biofilm on the electrode surfaces (Fig. 2C–D), which partly clogged the porosity of the felt electrode. This surface biofilm can explain the weak biofilm penetration in the felt. A previous study has shown that bioanodes formed on the same carbon felt provided current density as high as 80 A/m^2 in highly saline media (45 g/L NaCl) [19]. Such hard conditions led to the strong selection of halotolerant species, resulting in a biofilm mainly wrapped around the fibers inside the felt structure [20]. In contrast, in the chemically rich medium used here, the non-selective conditions led to the easy formation of a surface biofilm that hindered deep internal colonization and explained the modest performance of the 3D felt.

This result is similar to that reported recently with pure cultures of *Geobacter sulfurreducens* [15]. Activated carbon was compared to graphite felt and, unexpectedly, the surface area of the electrode material proved to have negligible influence on the electrochemical performance. The thick biofilm formed by *G. sulfurreducens* was assumed to be an element of the explanation [15]. This previous study, performed with a model system, and the present work, carried out in close-to-industrial conditions, similarly evidenced that the biofilm pattern is a major parameter controlling the bioanode performance. The biofilm pattern can annihilate the advantage of 3D porous electrodes that has been postulated a priori so far. This issue now deserves dedicated investigations.

4. Conclusion

Bioanodes were formed in wastewater used as the medium and fed with food wastes. In this context, 2D cloth performed similarly to 3D felt. The higher efficiency of 3D electrodes, which has generally been postulated a priori so far, should now be called into question depending on the operating conditions. The study has shown that the biofilm pattern is a major parameter that controls the electrochemical performance and can annihilate the advantage of 3D porous electrodes. In industrially-scalable conditions, 2D electrodes should now be considered as a worthwhile solution, particularly with the objective of subsequently designing multilayer electrodes.

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