Long-term experience in anoxic wastewater treatment plants of planar MFC with Ce-doped cathodes

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Abstract. Planar MFC prototypes were constructed and experimented to operate as sensors of the anoxic condition in a denitrification tank of a wastewater treatment plant in Italy, during different times in 2018 – 2019. Electrodes were differently enriched with carbon paint containing nanotubes and CeO2 nanoparticles. Performances of different electrodes were compared. Results underline critical anoxic conditions in the tank, that caused a very low signal and phenomena of signal reversion during some period of the year. the activity of aerobic microorganisms and protozoa growing and grazing the bacteria on the electrodes strongly influenced the signal of the MFCs. The presence of nanoceria enhanced, for some extent, the MFC signal, both in presence of reversing trends and in absence of these phenomena. In absence of reversing trends, nanoceria enhanced the MFC voltage. Such signal trends from MFCs can give, in real-time, useful information to optimize the purification process without the necessity of frequent biological and chemical analyses.

1 Introduction

Microbial fuel cells (MFCs) have been extensively proposed as a valid alternative to traditional sensors for the wastewater treatment providing a comparatively cheaper and faster solution, showing high linearity, stability, and good reproducibility [1]. In fact, the electro-active microbial biofilm on electrodes can work as a low-cost quantitative biological recognition element, directly converting biochemical energy to bioelectricity, through the metabolic activity in the biofilm. However, long-term testing of microbial fuel cells in wastewater plant were seldom documented.

Previous works documented the performance of planar MFCs, demonstrating their capability of returning a signal related to physical and chemical parameters of the environment, such as light, temperature and dissolved organics [2-4]. In continuity with previous experiences carried out in Italian wastewater plants [2, 3], sets of microbial fuel cells of planar geometry were carried in a different wastewater plant (CAP Group, wastewater plant Bresso, Italy), and using different carbon electrodes for the cathode.

Electrodes were enriched with carbon nanotube, Ce-doped and/or undoped. CeO_2 nanoparticles were added through a Ce doped carbon-based powder, aiming at forcing more aerobic condition on the cathode than in undoped carbon cloth ones, to improve the intensity of the signal. Indeed, previous lab tests with Ce-doped cathodes of air breathing cathodes in single chamber microbial fuel cells demonstrated an improved performance of the electrochemical system [4], induced by the presence of Ceria nanoparticle in the air cathode. The results of monitoring in anoxic tank of the wastewater plant is here compared, aiming at the monitoring of the process during different period of the year.

2 Materials and methods

2.1 Planar MFC setup

Several triplicate sets, composed of three planar MFC prototypes, were constructed and operated in the anoxic tank of the wastewater treatment plant of Bresso-Niguarda (group CAP Amiacque, Milan, IT) during different times in 2018 – 2019 (Figure 1 and Figure 2).

The planar prototype (Fig. 1) consists of two planar electrodes separated by a polypropylene felt of 1 cm, as a sandwich, attached to a structural floating frame. The floating frame, made of polystyrene, ensured to keep a planar structure of electrodes on the water surface. In this way, one of the electrodes faces the air, while the other faces the anoxic water. The porous felt assures the wet condition for both electrodes. The same construction of floating MFCs has already been tested in previous experiments in other wastewater plants [2, 3].

For the first test performed at the beginning of 2018, the submerged anodes and cathodes were made of pristine carbon cloth (CC) (10x10 cm, SAATI P10). The same carbon cloth differently enriched with carbon nanotubes and used for anode of the subsequent tests (2018-2019). Cathodes and CeO_2 nanoparticle were added on the cathodes for those tests. A carbon paint enriched with nanotubes (Vernici Bresciane, Italy) were used to cover a face of the carbon cloth. CeO_2 nanoparticles were spread on the paint. MFC with cathodes characterized by Ce-nanoparticle and carbon nanotubes are labelled cathode Ce-Nt, the other MFCs without nanoceria particles in the cathode are labelled cathodes NT.

The electrodes were connected to an external circuit with 100 Ω load and separated by an insulating polypropylene felt attached to the frame (Figure 1).

The voltage was continuously measured using a multichannel Data Logger (Graphtech midi Logger GL820).

Figure 1. Planar MFCs floating in the anoxic tank of the wastewater plant during the test. The schematic of MFC components is reported right on the top.

2.2 SEM micrography of electrode samples

Electrode samples were collected to analyse the biofilm structure and nanoceria permanence.
First of all, the electrodes were washed in sterile Phosphate Buffered Saline (PBS, 0,1 M, pH 7.4) to remove the non-attached bacterial cells. For biofilm fixation, electrodes were incubated overnight at room temperature in new sterile PBS containing 2% glutaraldehyde.
To achieve dehydration, samples were washed two times in sterile water, sequentially treated with 30, 50, 70 and 96% of ethanol solution baths at 10 minutes intervals and infiltrated with 30, 60 and 100% of HMDS (hexamethyldisilazane). After this, electrode pieces were air dried and finally sputter coated with a thin layer (about 10 nm) of gold to produce a conductive surface. SEM-SE imaging was performed using Zeiss Gemini 500 operating with an acceleration voltage of 5 kV.

3 Results

The average of the voltage of each type of planar MFCs operated at Bresso wastewater plant during different period of time is shown in the graphics of Figure 2.

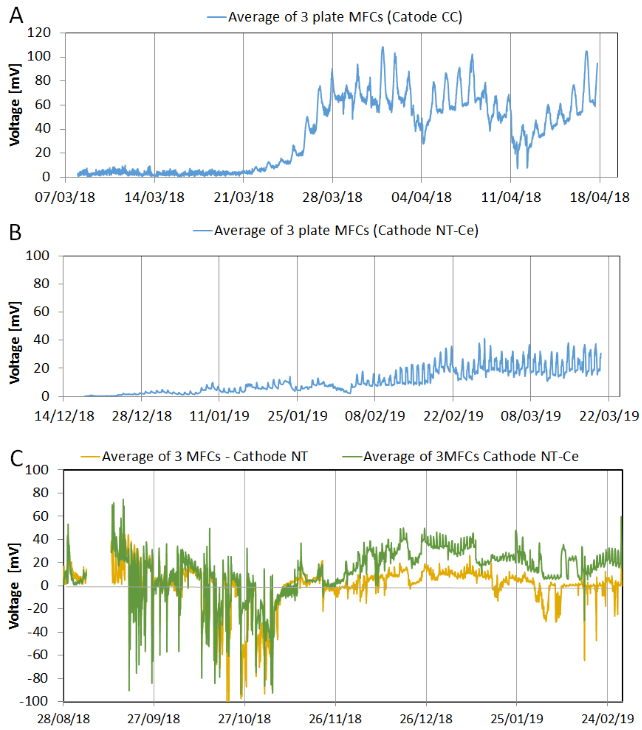


Figure 2. Voltage of planar MFCs (average of three replicates) operated at Bresso wastewater plant. A: anodes and Cathodes of carbon cloth (CC); B: anode of CC and Cathode of CC+NT+Ce; C: anode of CC+NT and cathode in CC+NT or CC+NT+Ce.

Figure 2 shows the signal trends (voltage) of the floating MFCs in the different tested configurations. In the first trial with CC anodes and cathodes made of pristine carbon cloth (Fig. 2A) we observed a typical lag phase of two weeks at the beginning of the test when the bacterial colonization of the electrodes occurred. The signal started to increase after two weeks and was characterized by regular peaks reflecting day and night periods. The dependence of the signal magnitude with temperature could be due to the increased microbial activity at higher temperatures. Conversely, the light effect could be due to the stimulation of oxygen production by phototrophic bacteria, and algae, at the cathode. These signal patterns reveal that the magnitude of the signal could be affected by other variables than the organic load of the water. A similar pattern was observed in the experiments with the cathode functionalized with NT and Ce (Fig 2 B) where a longer lag phase occurred before the signal started to rise. Therefore, the design of this floating biosensor should aim at minimizing the effect of external parameters.

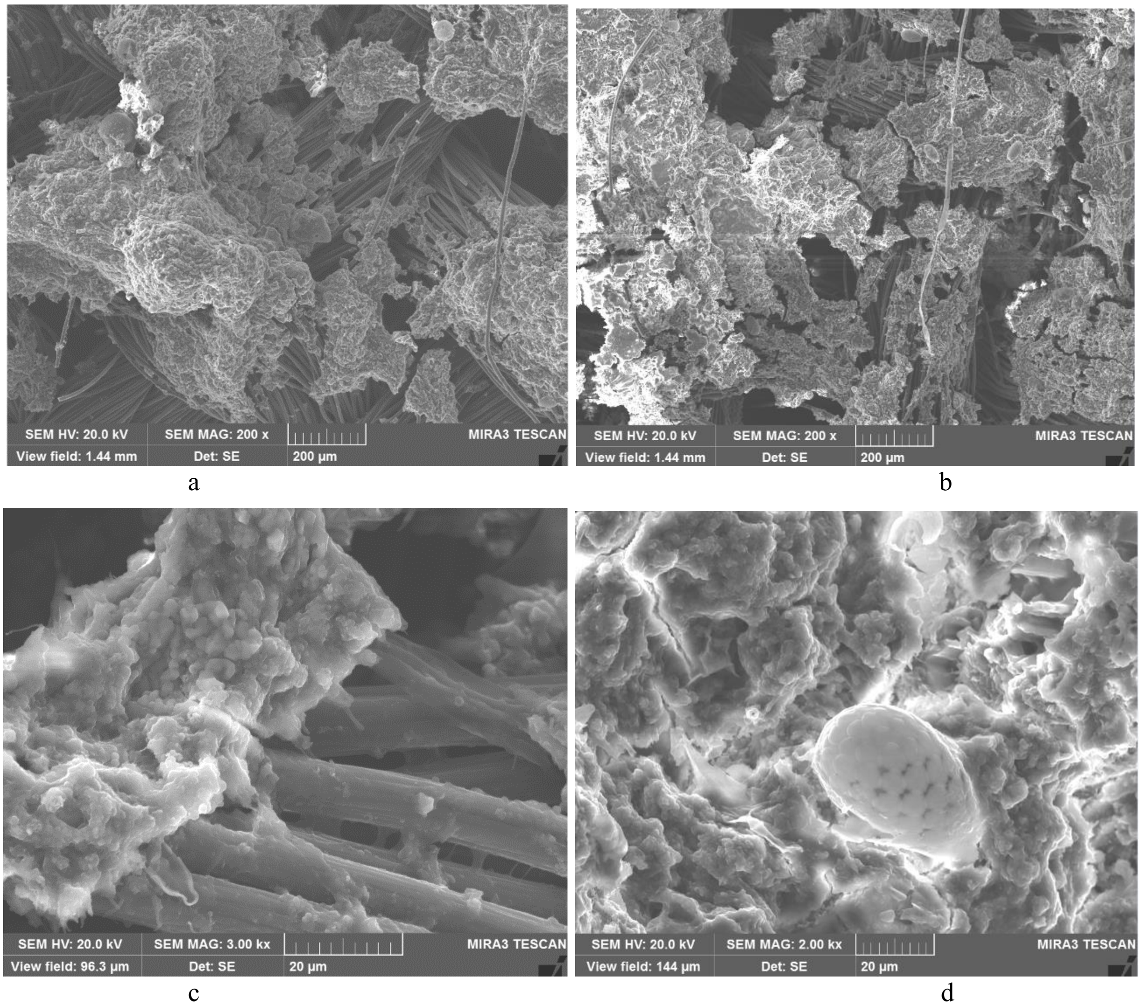
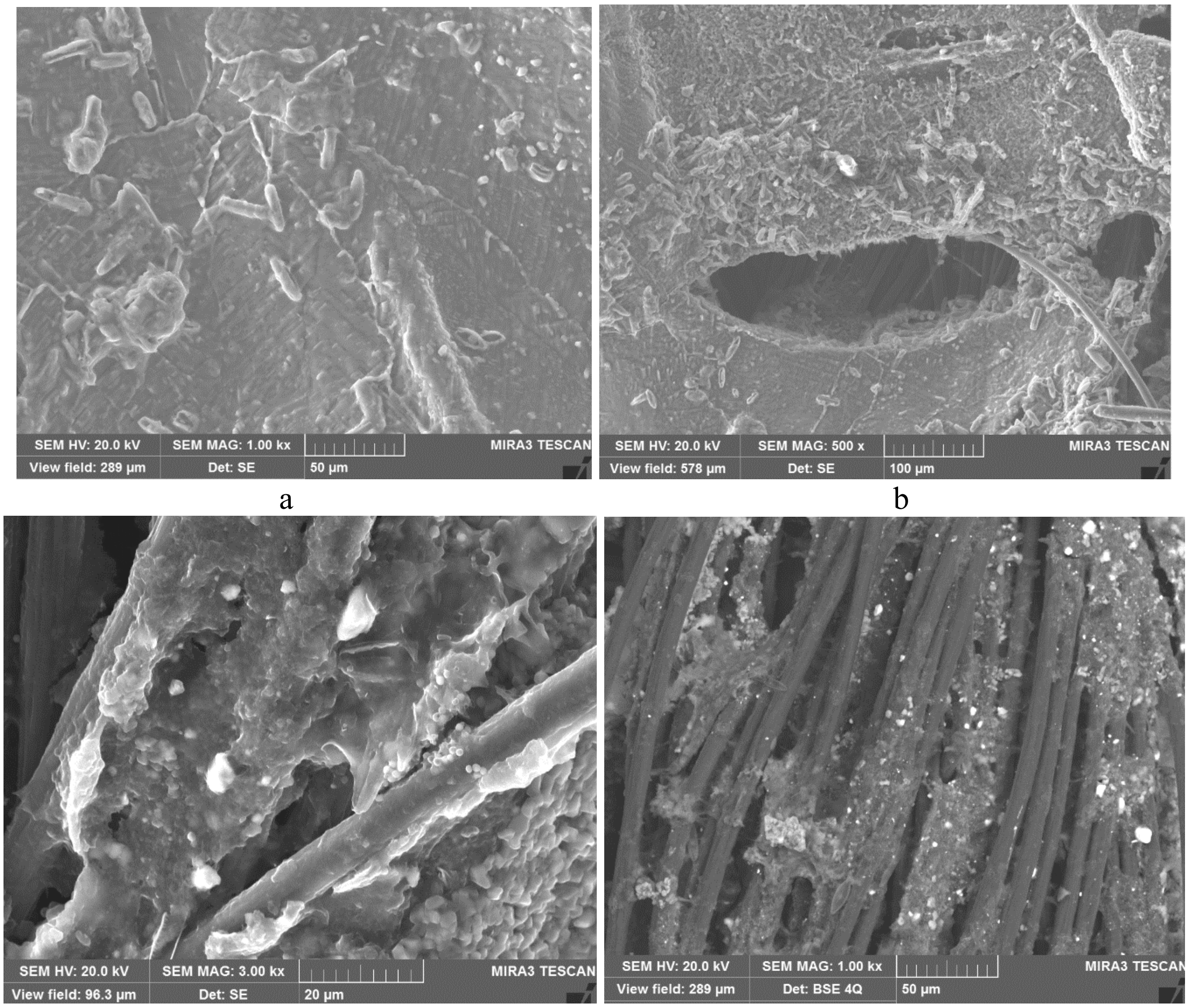


Figure 3. SEM micrographs at differnt magnitudes of biofilm on carbon cloth anodes enriched with carbon paint (CC-NT) (a-b). Details evidencing diatoms are visible in (c) and one protozoa of order *Euglyphida in (d).*

In the cell with the anodes functionalized with NT, particularly in the first part of the test, a significant inversion of the polarization of the electrodes with respect to that expected (Figure 2) was recorded. In other terms, the submerged electrodes acted as the cathode (instead of the anode), receiving the electrons from the air-exposed electrodes. This inversion of polarization documents the presence of oxic conditions in the first layer of the denitrification tank. Indeed, the measured profiles of redox potential and dissolved oxygens (data not reported) indicated that in the first centimeter of the water column oxygen is detectable and redox conditions are positive.

The oxic conditions are also witnessed by the presence of diatoms and amoebae, as the results of SEM analyses (Fig. 3). Particularly, among the visualized amoebae, SEM images allowed identifying some organisms belonging to Order *Euglyphida*, which are known to feed on bacteria. This surely has further reduced the potential electroactive bacterial communities on the submerged electrodes. Conversely, on the air-exposed electrodes, the development of oxygen-consuming bacterial biofilms should enhance anoxic conditions close to the electrode. The condition of anaerobiosis on the cathode was clearly documented in the previous lab works performed with single-chamber MFCs equipped with cathodes of carbon cloth enriched with a microporous layer of carbon powder [5, 6]. Indeed, in other similar lab MFCs tests [4] nanoceria boosted the performance of such cathodes acting as oxygen reservoirs beneath a well-established anaerobic biofilm.

The supposed mechanism of nanoceria was shorting distance between the electrode (electron donor) beneath the biofilm and the final electron acceptor (oxygen) outside the biofilm. Differently, here, the presence of nanoceria could have contributed to impeding the formation of an anaerobic biofilm, supplying further energy (oxygen and electron) to the oxygen-consuming bacteria and algae living on the cathode surface. This hypothesis is supported by the SEM images of cathodes in Figure 4. Observing the surface of the cathode CC-NT in Figure 4a-b, it evidently appears a thick layer of biofilm mixed to the nanotube coating above the carbon cloth base material.



a b

c d

Figure 4. SEM micrographs at differnt magnitudes of biofilm on carbon cloth cathodes : enriched with carbon paint CC-NT (a-b) and also doped with nanoceria CC-NT-Ce (c-d).

A crowd of diatoms appears on the surface, which was not able to penetrate in deep, reaching the carbon cloth fibers. On the contrary, the coating is disaggregated and patchy on the sample of cathode CC-NT-Ce (Fig. 4c-d). In this case, traces of diatoms are clearly visible close to the carbon cloth fibers.

The presence of diatoms was similar as in some of the anodes (Figure 3c).

Similar aerobic conditions, therefore, persisted (and evolved in time) on the anodes as well on the cathodes, inhibiting the raising of the voltage in the MFCs. Hence, this phenomenon induced in some period the reversing of the polarity between the electrodes.

The inversion of polarization occurred mainly in the warmest months (September-October) when the bacterial growth on the air-exposed electrodes is favoured. In this first part of the test, no differences between Ce-doped cathode and non-doped cathode were observed. Conversely, in the second part of the test (November-February), the expected polarization was observed for most of the time, although the signal was lower than that in previous experiments (ref o graph). It is worth mentioning that, in this period, Ce-doped electrodes showed higher signal than non-doped ones, which underwent polarization inversion only in the last month of the test. Thus, we can suppose that in the Winter period grazing protozoa were inhibited by the low temperature, as well as photosynthetic organisms, facilitating more anaerobic conditions on both the electrodes. In this last condition, nanoceria might have enhanced the cathode performance, increasing the cathodic potential. These allowed to record a correlated signal to the organic load dispersed in the wastewater tank. To validate and confirm the achieved results, further experimentation with different types of MFC and geometry is suggested. Nonetheless, it is worthy to note the versatility of simple MFC such as the one tested here, which signal can give useful information on the biology occurring in the wastewater process, as well as on some physical-chemical parameters and nutrients, in real-time.

4. Conclusion

Planar and membraneless MFC with carbon cloth electrodes differently enriched and doped with carbon Nanotube, Ce-doped, and/or undoped, were tested. The results indicated that in absence of a strong anoxic condition in the tank, cathode and anode tend to reverse.

The weak anoxic condition in the tank was documented by the presence of a rich flora of protozoa in the water, that inhibit anaerobic conditions on the anode by grazing microorganisms. MFCs signal stays very low, independently of the season of the year, and tend to reverse when anoxic conditions are not well stabilized. The presence of nanoceria at the cathode enhances the voltage of the MFC but also the phenomenon of signal reversing, probably favouring the life of aerobic protozoa which scratch the surface of the electrode grazing bacteria and biofilm. Signal trends from such MFCs can give, in real-time, useful information on the biology occurring in the wastewater, as well as on physical-chemical parameters and nutrients which are strategic to optimize the purification process.

4. Acknowledgements

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