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**Official URL:** [https://doi.org/10.1016/j.elecom.2019.05.022](https://doi.org/10.1016/j.elecom.2019.05.022)

**To cite this version:**
Hoareau, Morgane and Erable, Benjamin and Bergel, Alain *Microbial electrochemical snorkels (MESs): A budding technology for multiple applications. A mini review.* (2019) Electrochemistry Communications, 104. 106473. ISSN 1388-2481

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Microbial electrochemical snorkels (MESs): A budding technology for multiple applications. A mini review

Morgane Hoareau⁎, Benjamin Erable, Alain Bergel

Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INP, UPS, Toulouse, France

ARTICLE INFO

Keywords:
Microbial fuel cell
Electroactive biofilm
Wastewater treatment
Bioremediation
Conductive biofilter
METland

ABSTRACT

A microbial electrochemical snorkel (MES) is formed by the direct coupling of a microbial anode with a cathode, which may or may not be biotic. It can be considered as a short-circuited microbial fuel cell. In comparison with a microbial fuel cell, an MES does not produce power but it ensures the highest possible electrochemical reaction rates that the system can support. Although MESs have recently received little research attention, a multitude of possible applications have emerged in the last few years. MESs have recently been shown to be effective for organic matter abatement in wastewater, nitrate removal, decontamination of hydrocarbon-polluted sediments, and soil bioremediation. Other applications are foreseen. Thanks to its extreme simplicity, the MES could offer a real opportunity for short-term scale-up. This mini-review seeks to attract the attention of the research community to the potential of this technology and to propose research to develop it.

1. Introduction

The discovery of the electrocatalytic properties of microbial biofilms has raised great hopes for the emergence of microbial electrochemical technologies in various fields [1]. The microbial electrochemical snorkel (MES) is a very simple, probably the simplest, example of microbial electrochemical technology. It consists of the direct coupling of a microbial anode with a cathode, which may or may not be biotic [2]. In other words, it can be considered as a short-circuited microbial fuel cell (MFC) [3].

MESs were not the subject of much research in the years following their discovery in 2008 [4] and the first paper devoted to them [2], which was published in 2011. In contrast, several groups have recently implemented different versions of MESs and achieved success in a wide range of applications, including nitrate reduction [5], hydrocarbon removal [6,7] and wastewater treatment [8], and even relating to biogeochemical cycles [9]. Thanks to their extreme simplicity, the use of MESs is one of the microbial electrochemical technologies that could offer the opportunity of large-scale development in the short term. This review is intended to attract the attention of the research community to this technology and to propose lines of action to boost short-term MES scale-up.

2. MES principle, benefits and expectations

 Basically, an MES is a short-circuited MFC. MFCs are characterized by a bell-shaped power–current curve (Fig. 1). When short-circuited, an MFC no longer produces any power, because the voltage between anode and cathode is zero, but it works at the maximum possible current. The main advantage of an MES is thus to sustain the maximum current between cathode and anode that an MFC can produce. The reaction rates are raised to the maximum that the system can support. This way of operating is ideal when the objective is to raise electrochemical reaction rates rather than to produce electrical power. This is the case when the primary objective is the abatement of organic matter in wastewater [3], the decontamination of sediments or soils [10], the cleansing of effluents [11], the recovery of metals [12], etc. Actually, to be pragmatic, the power density produced so far by MFCs is so low that working in MES configuration should be the most suitable solution for many applications.

Another major advantage of an MES is the simplicity of the configuration it allows. A single conductive rod that spans two zones with different chemical compositions can be sufficient, for example, a carbon rod partially planted in anaerobic sediments with the upper part exposed to aerobic water (Fig. 1). An electroactive biofilm develops on the surface embedded in the anaerobic zone and releases electrons to the material. Electrons flow to the aerobic part, where they are transferred to oxygen. Such simplicity ensures low-cost and low-maintenance systems.

It has been noted that an MES can be seen as a process that mimics cable bacteria [7,13]. Cable bacteria are filamentous bacteria contained...
in marine and freshwater sediments, which can transport electrons over centimetre-long distances, for instance from anoxic sediments where sulfide is oxidized to the aerobic layers above where oxygen is reduced. The fact that MESs operate in a similar way to a natural process is an additional reason to be optimistic about their capacity for adaptation to large-scale applications.

A very wide range of applications is anticipated. The capacity of MESs to enhance wastewater treatment [2,8], remediation of hydrocarbon-contaminated sediments [6], and nitrate [5] or sulfate [9] removal have already been demonstrated experimentally. It has also been speculated that using MESs in landfills or wetlands may divert electron flow from methane production in the anaerobic zone and thus offer a strategy for preventing methane emission [14]. Benthic MESs may be able to shift microbial respiration patterns in soils and sediments. The increase in redox potential associated with electron transfer via MESs may be a way to mitigate other environmental concerns, such as the production of sulfide and mercury methylation, and to improve the cultivation of crops such as rice [14].

3. MES applications

3.1. Abatement of organic matter in wastewater treatment

The seminal paper demonstrated the efficiency of an MES in reducing organic matter in wastewater [2]. An MES was compared with a 1000 Ω-connected MFC and a control without electrodes. COD decreased by only 15% in the control, while the abatement was 40 to 50% with the MFC and reached 60 to 75% with the MES.

The most impressive successes have been obtained by implementing MESs in a constructed wetland, resulting in a so-called Electroactive Biofilm-Based Constructed Wetland (EABB-CW) [15]. In this case, MES is used as a kind of conductive biofiltration bed integrated in an artificial lagoon. Compared with a conventional lagoon equipped with gravel, an MES using conducting coke granules ensured COD and BOD₅ reductions up to 3 times and 4.5 times higher, respectively [8]. The MES made it possible to reach the discharge limit values of 125 mg O₂·L⁻¹ for COD and 25 mg O₂·L⁻¹ for BOD₅ after the very low retention time of 0.5 day, while the control equipped with gravel only reached this legal limit after a retention time of 3.4 days. Further studies on EABB-CW have shown the impact of the nature of the conductive material on the capacity of the MES to remove pollutants [17,20].

For the treatment of pig manure, COD removal of up to 90% was attained, while the control equipped with a sand biofilter gave 81% [16]. EABB-CW was also efficient for ammonium and phosphate removal [16].

3.2. Denitrification

An MES was used to reduce nitrates. The anodic part, made of carbon felt, was set in sediments and the cathodic part, an iron cylinder, was in the solution above, which contained sodium nitrate. The anode oxidized organic matter, while the cathode reduced nitrate to N₂ [5].

This MES was compared with two control reactors, one containing only sediments with no electrode, and the other only the electrode without sediment. From the 5th day, a rapid decrease in nitrate was observed with the MES, whereas its concentration did not vary in the control reactor without sediment and decreased only slightly from the 10th day in the reactor with no electrode. After 16 days, the nitrate removal efficiency in the MES reactor reached 98%. However, a green rust-like surface coating was observed on the iron rod (cathode part), so the mechanism of nitrate reduction may not be a simple electrochemical reduction on the cathode, but could also involve chemical reactions with iron.

3.3. Hydrocarbon biodegradation

Several studies have proposed the use of MESs to decontaminate marine sediments polluted with hydrocarbons. Experiments were conducted over 400 days with reactors containing one or three snorkels. Control experiments were performed without a snorkel or with a snorkel but in an autoclaved medium [6]. The snorkel consisted of a simple graphite rod with the lower part immersed in crude-oil-contaminated sediments and the upper part in the aerobic water above.

No change was observed after 200 days for the control without snorkel. The reactors equipped with one and three snorkels showed a decrease of 12 and 21%, respectively, in the total petroleum hydrocarbons. After 417 days, there was no significant difference between controls and snorkels. In this case, the snorkels accelerated the biodegradation and were less expensive than conventional treatments.

A similar experiment conducted on hydrocarbon-contaminated sediments from a river led to the modelling of the chemical and biological reactions involved in MES process [9]. The MES mainly accelerated sulfate reduction driven by the oxidation of the organic contaminants.

The bacterial populations on the MES surface had a configuration similar to those found in marine sediments, with a majority of Proteobacteria (85% for the electrode, 61% for sediments) [7]. However, Alphaproteobacteria, including sulfur- and sulfide-oxidizing bacteria which may be capable of transmitting the electrons resulting from sulfide oxidation, were mainly present on the electrode surface, while the sediments contained a majority of Deltaproteobacteria. The snorkel has been suspected of having an impact on microbial communities, even those far from its surface, and of stimulating biodegradation by sulfate-reducing bacteria in the surrounding area [21].

3.4. Soil bioremediation

In flooded soils, a deficiency of suitable electron acceptors can limit the efficiency of microbial remediation of organic pollutants. Conventional bioremediation techniques overcome this constraint by supplying additional electron acceptors like oxygen (bioventing) or nitrates [22]. This process can raise some concerns in terms of cost and secondary pollution, e.g. by nitrite [23]. Alternatively, electrons can also be supplied by using electrodes in so-called microbial electro-remediating cells [24] or a bioelectroventing process [19].

A recent paper has compared a bioelectroventing process with other electro-microbial processes, including MES, for ¹⁴C-ATR mineralization, i.e. complete degradation of ¹⁴C-aztrazine to ¹⁴CO₂ [19]. The snorkel consisted of a graphite felt electrode placed vertically, partially buried in soil and partially surrounded by the water above. A control
experiment was performed with one electrode buried in soil and another in the water above, but not connected. After 20 days, the toxicity of soils treated (measured by the inhibition of Pseudokirchneriella subcapitata algal growth) was 20% in the snorkel and 45% in the control. Nevertheless, zero toxicity was obtained only when the anode was polarized at 600 mV vs. Ag/AgCl using a 3-electrode set-up.

4. Perspectives

Several possible application domains of MESs have been considered, mainly relating to waste treatment and environmental remediation. The application horizon is already wide but could be further extended to other sectors, such as metal recovery.

EABB-CWs have revealed promising capabilities, not far from practical applications in the short term. This success may be linked to the high surface area-to-volume (A/V) ratio (Table 1), which resulted from implementing the snorkels in the form of a packing bed. In contrast, most other studies found low A/V ratios. Consequently, it would be advisable to work with the highest possible A/V ratios in future research to assess the full capabilities of MESs.

Generally, the potential at which an MES works is not reported in the literature. This is a serious omission because the potential is the main parameter by which the snorkel can affect the electrochemical reactions that happen on its surface. As a first simple approach, the distribution of the electrostatic potential in solution can be neglected, assuming thus that the snorkel works at a uniform Nernst potential. If the kinetics of the anode and cathode parts are known, the Nernst potential of the snorkel can be calculated by determining the value at which the anode current is equal to the cathode current (Fig. 2A). Moreover, the working potential of the snorkel can be controlled by adjusting the ratio of anode to cathode surface areas. Increasing the cathode surface area will move this potential towards higher values, while, conversely, increasing the anode surface area will decrease it. Practically, the snorkel potential could thus be controlled dynamically by designing a system with several anode and cathode parts, connected together through simple on/off switches (Fig. 2B).

The relative surface areas of the anode and cathode could thus be adjusted by simple connection/disconnection of the various parts.

To advance the snorkel design, ion transport in the vicinity of the snorkel should be modelled numerically in order to assess the potential distribution along the snorkel surface [25,26]. Such a calculation will help in the design of the optimal snorkel architecture. It can be anticipated that the snorkel will mainly be efficient in the vicinity of the interface between the anode and cathode zones [14]. Ion transport modelling should consequently be primarily helpful in determining the required snorkel length and the appropriate configuration on both sides of the interface. In combination with numerical modelling, fundamental studies with pure cultures should be helpful to decipher the MES mechanisms [11].

Snorkels can be made of a single conductive material, which is exposed to two zones that determine the cathode and anode areas (Fig. 1). In this case, the two zones are often not accurately delimited but correspond to the oxygen concentration gradient with depth. The biofilm must consequently catalyse organic matter oxidation when close to the oxygenated zone. The emerging research on air-to-labolant or aerobic microbial anodes [27,28] should be very helpful in optimizing such an MES. If the interface between the two zones varies, due to variable reactor filling or waves in a natural environment, the biofilm should be alternately electrically active (anode) and electrotrophic (cathode). Recent research on reversible, also called bidirectional, microbial electrodes [29,30] should provide useful basic inputs.

MESs can also be designed by combining two materials, one promoting the formation of an anode and the other the formation of a cathode (Fig. 2) [25,26]. Nevertheless, so far, it has been necessary to locate each electrode in a zone with different chemical composition. This situation may be overcome, according to a recent study that has demonstrated that anodic or cathodic electroactive biofilms can be formed in exactly the same medium, at exactly the same potential, depending only on the electrode material [31]. On this basis, a new kind of MES can be imagined, which would be able to work in a single phase. This monophasic MES would have to couple two different conductive materials able to promote the development of an anode and a cathode in the same medium.

5. Conclusion

MESs have given rise to great expectations in many important
application areas and real successes have started to appear. Despite this, the number of studies still remains very small. These early successes emphasise the urgent need for research endeavours in this field. The similarity of the concept with self-organized cable bacteria further adds to the belief that the guiding idea is solid and should lead to basic discoveries beyond the scope of the practical applications contemplated so far.

Acknowledgements

This work was supported by the French Agence Nationale de la Recherche (ANR), within the framework of the Biotuba project (ANR-17-CE06-0015).

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