Biomimetically Generated Nanoparticles in Boosting the Performance of Microbial Fuel Cells

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ABSTRACT

Studies are presented in the context of the past attempts at finding nanocatalysts that can boost the performance of microbial fuel cells (MFCs) — in terms of waste treatment and energy generation. Given the great potential of biomimetically synthesized nanoparticles (BMNPs) in providing less expensive and more environmentally friendly alternatives to NPs synthesized by physical and chemical methods, as well as a near-total lack of previous work in this area, the current research was undertaken. Effect of gold and silver nanoparticles (NPs), synthesized biomimetically using five freely available weeds, was assessed as catalysts in the MFCs. In all cases, the nanoparticles were seen to enhance the coulombic efficiency (reflective of the reduction in the waste's organic carbon load), maximum attainable power density, and overall energy yield of the MFCs by >200% relative to the uncatalyzed MFCs. Gold nanoparticles were more effective than silver nanoparticles by ≥ 20%. The results reveal that biomimetically synthesized NPs can be highly effective in reducing the operational costs as well as ecological footprints of MFCs and further work should be focused on NPs of non-precious metals.

INTRODUCTION

The Economic Unviability of Microbial Fuel Cells (MFCs) and the Need to Remedy it

As reviewed by us recently (Tabassum-Abbasi et al. 2019), microbial fuel cells (MFCs) have been explored extensively in recent years for the dual objective of generating energy while treating organic waste. Despite having aroused expectations that they may provide an avenue for waste cleaning as well as energy production (Moqsud et al. 2013, Rahimnejad et al. 2015, Kumar et al. 2018), MFCs have not become economically viable due to their high cost, added to their significant ecological footprint. Life cycle analyses have shown time and again that from their birth to decommissioning, MFCs consume much more energy than they generate (Tabassum-Abbasi et al. 2019). For this reason, most contemporary research on MFCs is devoted to improving their economic viability by reducing their fabrication and operational costs along with improving their efficiency (Kodali et al. 2018, Palanisamy et al. 2019).

Factors that Have Led to the Exploration of Nanoparticles

The ability of an MFC to treat wastewater and generate energy is directly influenced by the rate at which redox reactions take place in its substrate (Rodrigo et al. 2007, Rittman et al. 2008). During the initial phase of MFC research, compounds called ‘mediators’ – which could induce electrons to come out from the cells of growing microorganisms and supply them to the anode – were tried to boost the redox reactions. But the mediators turned out to be either toxic to the microorganisms or were too expensive to be viable, or both (Mustakeem 2015, Santoro et al. 2017).

The next emphasis was on the use of catalysts, abiotic as well as biotic. Abiotic catalysts, based either on platinum group metals (PGMs), or other metals (OMs), have since been explored extensively (Noori et al. 2020). However, PGM catalysts are not only expensive but they may also be poisoned, which is a problem in MFCs that use wastewater as a source of energy. The OM catalysts, especially carbon-based ones, have shown greater resistance towards deactivation (Firdous et al. 2018, Palanisamy et al. 2019), but their catalytic efficiency has not been adequate (Pan et al. 2016, Santoro et al. 2017).

This background has prompted efforts on the use of nanoparticles in speeding up the redox reactions occurring in the MFCs. Nano catalysts derived from platinum group metals (PGMs), other metals (OMs), and non-metals (NMs), have been explored. The reports published so far on these catalysts have been reviewed by Rajalakshmi (2019) and Noori et al.
Besides single-element NPs like AgNPs, the NPs of silver, gold, manganese oxide, titanium oxide, vanadium pentoxide, etc., either coated upon or in general modified with carbon paper or nanotubes, have been explored in enhancing the waste reduction and energy generation capabilities of MFCs (Naruse et al. 2011, Alatraktchi et al. 2012, Kalathil et al. 2013, Noori et al. 2016, Sui et al. 2017, Zakaria et al. 2018). All the studies have indicated a beneficial effect which makes a strong case for exploring the use of BMNPs so that similar or better benefits can be achieved but at much lesser costs and much greater eco-friendliness. This report is a step in that direction.

The Present Work

In the present work, we have explored the use of AgNPs and AuNPs, in boosting MFC performance. The NPs were biomimetically synthesized using aqueous extracts of obnoxious and freely available weeds lantana (Lantana camara), water hyacinth (Eichhornia crassipes), mimosa (Mimosa pudica), parthenium (Parthenium hysterophorus), and coral vine (Antigone nepetopus). No past report of this kind is available. Another highlight of this study is that the MFC chambers were linked through a salt bridge rather than a membrane, as most other authors have done. We have done this switch because membranes are not only costlier than salt bridges by several orders of magnitude but also cause a much greater burden on the environment than the salt bridge during their manufacture and decommissioning. Even otherwise, whereas membranes have some advantages in comparison to salt bridges, they are also besieged with serious drawbacks (Rajalakshmi 2019).

MATERIALS AND METHODS

Duel-chambered MFCs of 1500 mL capacity were fabricated with 3 mm thick plastic (Fig. 1). The chambers were linked via a salt bridge, containing agar (3%, w/v) and NaCl (10%, w/v). Twenty-two such units were deployed.

The energy source was an aqueous solution of glucose (1 g.L⁻¹), inoculated with 0.1 g.L⁻¹ fresh cow dung as the microorganism source. Phosphate buffer (100 mm) was used as the catholyte. The electrodes comprised copper rods with a surface area of 8.5 mm².

The MFCs

The anodic chambers were sealed with an epoxy resin to maintain anaerobic conditions. It was possible to do it because the MFCs were operated in batch mode. Otherwise, for continuously operated MFCs, it is necessary to provide feed inlet and CO₂ outlet in the anode chamber. On the other hand, the aerobic atmosphere was ensured at the cathode chamber by providing a hole at its top for the passage of air.
All the units were housed in a common room so as to be at identical temperature (30 ± 4ºC). Two of the MFCs were used as controls. The MFC voltage was recorded using a Haoyue (DT 830D) digital multimeter. The other 20 MFCs contained duplicate sets spiked with AuNPs or AgNPs synthesized from the corresponding weeds, as shown in Table 1. Adequate quantities of the NPs were added to the catholyte to attain a concentration of 0.02 mg.L⁻¹ in the catholyte solution.

**Quantifying MFC Performance Indicators**

Besides peak voltage (PV), the other MFC performance indicators were computed as follows.

**Maximum power density (MPD)**

\[ \text{MPD} = \frac{\text{Power}}{\text{Electrode surface area}} \, \text{mW/m}^2 \]

**Coulombic efficiency (CE)**

\[ \text{CE} = \frac{\text{Ci} - \text{Cf}}{\text{Ci}} \times 100, \, \text{as} \% \]

Where Ci and Cf represent Ci-initial COD (mg.L⁻¹) and Cf-final COD (mg.L⁻¹).

**Total energy output (TEO), in watts**

\[ \text{TEO} = \int_{t_i}^{t_f} P(t) \, dt \]

Where P is power and was obtained by measuring areas under the wattage-time curves of which a typical one is shown in Fig. 2.

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**RESULTS AND DISCUSSION**

The results are summarized in Table 1. The information has been presented in terms of a) the peak voltage (PV) which reflects the maximum deliverable power by an MFC; b) the coulombic efficiency (CE) which is a measure of the ability of the MFC to treat the given organic waste, and c) the total energy generated by the MFC. Since the electrodes of all the MFCs had identical surface areas, the maximum power density (MPD) values are directly proportional to the PV values in the present investigation.

The control MFC could deliver a PV and a total energy output (TEO) of only 131 ± 2 mV and 20mW, respectively. But the use of either of the NPs boosted the PV by 5-7 times. The TEO was spiked to similar extents.

The AuNPs of all the weeds were seen to enhance the MFC performance to a greater extent than their AgNPs; the difference being statistically significant at > 99% confidence level. The order in which the nature of the weed influenced the PVs attained by the corresponding AuNPs was *L. camara > A. leptopus > E. crassipes > M. pudica > P. hysterophorus*.

The order for the PVs attained with AgNPs was similar except that the AgNP of *M. pudica* led to slightly better PV than the AgNPs of *E. crassipes*. The CE values, the MPD values, and the TEO essentially followed the order of the PV values.

Compared to the MPD of 145.5 mV.m⁻² attained in the lone previous report on the use of BMNPs in MFCs — by
using a Haoyue (DT 830D) digital multimeter. The other 20 MFCs contained duplicate sets spiked with AuNPs or AgNPs synthesized from the corresponding weeds, as shown in Table 1. Adequate quantities of the NPs were added to the catholyte to attain a concentration of 0.02 mg.L\(^{-1}\) in the catholyte solution.

**Quantifying MFC Performance Indicators**

Besides peak voltage (PV), the other MFC performance indicators were computed as follows.

- **Maximum power density (MPD)**: \(\frac{P_{PEPE}}{E_{EEEEE}} \times \frac{s_{PP}}{s_{PP}} \times \frac{E_{PP}}{s_{PP}}\), \(mWm^{-2}\)
- **Coulombic efficiency (CE)**: \(\frac{Ci-Cf}{Ci} \times 100\)%, \%

Where \(Ci\) and \(Cf\) represent \(Ci\) - initial COD (mg.L\(^{-1}\)) and \(Cf\) - final COD (mg.L\(^{-1}\)).

- **Total energy output (TEO)**, in watts: \(\int P_{PP} \cdot dP\) \(E_{EE2} \rightarrow E_{EE1}\)

Where \(P\) is power and was obtained by measuring areas under the wattage-time curves of which a typical one is shown in Fig. 2.

**Fig. 2:** A typical watt-time curve of the power generated by the MFCs used in the present study. This curve pertains to AuNP synthesized with the SLE of *A. leptopus*.

**Table 1:** Effect of gold and silver nanoparticles synthesized from 5 pernicious weeds on the efficacy of the MFCs. All the MFCs had anodes of 1500 mL capacity, and in each, MFC glucose solution (1 g.L\(^{-1}\)) and phosphate buffer solution (100 mm) were used as an anolyte and catholyte, respectively. Their copper electrodes were connected with a salt bridge.

| The plant utilized | NP Used | Peak voltage, (mV)* | Coulombic Efficiency, % | Maximum power density attained, (mW.m\(^{-2}\)) | Total energy output, (mW) |
|--------------------|---------|---------------------|------------------------|-----------------------------------------------|--------------------------|
| None               | -       | 131 ± 2             | 21                     | 23                                            | 20                       |
| *Lantana camara*   | Au      | 948 ± 3             | 80                     | 133                                           | 121                      |
| *Eichhornia crassipes* | Au | 916 ± 2             | 77                     | 129                                           | 114                      |
| *Mimosa pudica*    | Au      | 907 ± 3             | 78                     | 125                                           | 133                      |
| *Parthenium hysterophorus* | Au | 841 ± 1             | 68                     | 106                                           | 108                      |
| *Antigonon leptopus* | Au | 921 ± 2             | 66                     | 89                                            | 119                      |
| *L. camera*        | Ag      | 771 ± 3             | 59                     | 78                                            | 89                       |
| *E. crassipes*     | Ag      | 735 ± 1             | 59                     | 77                                            | 86                       |
| *M. pudica*        | Ag      | 741 ± 2             | 55                     | 74                                            | 87                       |
| *P. hysterophorus* | Ag      | 677 ± 2             | 51                     | 61                                            | 86                       |
| *A. leptopus*      | Ag      | 739 ± 1             | 53                     | 72                                            | 96                       |

*Average of duplicates

Harshiny et al. (2017), the maximum MPD attained by the MFCs in the present report is 133 mV.m\(^{-2}\). But these authors have used a salt bridge instead of a membrane. Its advantage in terms of lower cost and ecological footprint more than compensates for marginally lower MPD.

As for the comparison with past work on the use of NPs synthesized by chemical or physical methods in catalyzing MFCs, it is seen that the MPDs/PVs generated by our MFCs have been superior to the MFDs/PVs attained with those NPs in several cases. For instance, Kalathil et al. (2013), using a plain carbon paper modified with a composite of carbon nanotube (NT) and MnO\(_2\) NPs, attained an MPD of 120 ± 1.7 mW.m\(^{-2}\). Asghary et al. (2019), employing a carbon paste electrode (GPE), combined with CNT and AuNPs, achieved an MPD of 80 mW.m\(^{-2}\). Khajeh et al. (2020) electrochemically deposited CuO/ZnO NPs on a graphite cathode used in MFC to obtain an MPD of 51.9 mW.m\(^{-2}\). By using NPs of Cu\(_2\)O in conjunction with reduced graphene oxide cathode in their MFC, a PV of 223 mV was realized (Xin et al. 2020) in comparison to the PVs of 677-948 achieved by the authors in the current work.
Fan et al. (2007) had obtained an MPD of 74.4 mW.m\(^{-2}\) from MFCs spiked with AuNPs while in all the MFCs reported in this paper, the MPD values have been significantly higher at 89-133 mW.m\(^{-2}\).

As for coulombic efficiency, only nine of the past authors, as reviewed by Rajalakshmi (2019), have reported it. In six of those studies, the efficiencies obtained have been lesser than the maximum of 80% obtained by the present MFCs. Given that all the past authors have achieved enhancement in the performance of their MFCs using the highly expensive Nafion membrane, or a cation exchange membrane, we have attained the same using only the inexpensive salt bridge.

The work described in this paper is based on the BMNPs of Ag and Au because these two metals have been most extensively studied of all BMNPs. But further work should aim at the use of less expensive metals and metal oxides to bring down the MFC cost.

**CONCLUSION**

This paper has presented studies on the performance of biomimetically synthesized gold and silver nanoparticles (BMNPs), using the weeds lantana (*Lantana camara*), water hyacinth (*Eichhornia crassipes*), mimosa (*mimosa pudica*), coral vine (*Antigonon leptopus*), and parthenium (*Parthenium hysterophorus*) in boosting energy output from microbial fuel cells (MFCs). Dual compartment, batch fed, MFCs of 1500 mL capacity in which salt bridge was used as the electrode interface, were employed for the purpose. The study is the first of its kind because only one previous report exists on the use of BMNPs in enhancing MFC performance and none deal with the use of weeds, or salt bridge, or report overall energy yield.

It was seen that the NPs of both the metals with all the five weeds enhanced the MFC performance several times as compared to the control MFCs.

All the NP-spiked MFCs had peak voltage, coulombic efficiency, and energy output that were favorably comparable to the ones achieved by previous authors using NPs generated by chemical or physical means.

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