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NANO-BIOLOGICAL MODIFICATION OF THE ELECTRODES IN MICROBIAL FUEL CELL

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ABSTRACT

Recently, renewable energy with the ability to replace traditional energy such as fossil fuels, has attracted the attention of many researchers. In this study, the amount of the produced electricity in the presence of modified graphite electrode with biological synthesized silver nano particles was evaluated. In the first stage microbial fuel cell (MFC) system was designed; subsequently, synthesized silver NPs through biological method and their properties were investigated using UV-vis spectroscopy, Fourier transform infrared spectroscopy (FTIR) and particle size analysis (PSA). Scanning electron microscope (SEM) was used for exploring the modified electrodes with silver NPs and valid modification status. Eventually, the modified graphite electrode with used NPs and the amount of produced electricity in the presence of electrodes were evaluated. Our results showed that the modified graphite electrode with NPs has high potential for electricity generation that was more than bare graphite electrode. Indeed, the generated maximum power and current density for bare graphite electrode were 82 mW/m^{-3} and 1100 mA/m^{-3} respectively but the generated maximum power and current density for modified electrode with silver NPs were 160 mW/m^{-3} and 1400 mA/m^{-3} respectively.

KEYWORDS:
Nano-biological Modification, Microbial Fuel Cell, silver NPs

INTRODUCTION

Recently, due to the reduction of fossil fuel resources and the destructive effects of global warming, the use of biomasses as a safe, sustainable and optimal resource has been considered. In this regard, various studies have been conducted and different methods have been introduced [1]. MFC, considering the catabolic ability of microorganisms for generating electricity, is one of the most optimal approaches which was introduced for first time by Potter in 1911[2]. MFC is a combination of microbiology, electrochemistry and other compatible sciences such as nanotechnology that lead to transformation of chemical energy to electrical energy. In this system anaerobic microorganisms, by attaching to the electrode surface, create a complex structure that called biofilm. In biofilm structure, microorganisms are creating electrons by oxidizing organic matter. The produced electrons move among respiratory enzymes and participate in energy generation as ATP form. Then, after passing among the electrolyte in the cell, the electrons are transferred to electron acceptor (anode) and subsequently to electron acceptor in cathode. In addition, the produced positive ions in anode are conducted towards cathode by passing through the membrane (electrolyte); in the presence of catalyst, react with the oxygen and electron that reach the cathode section from the external circuit and are turned into water molecules (figure1) [3,4,5]. Different and complex parameters such as the type of cathode and anode, the rate of transfer electron, microbial biofilm anode, the rate of transfer electron from the anode to the cathode, the substrate used for biofilm formation, ohmic resistance of the electrolyte and the other factor chemical can be involved in MFC performance[6]. However, one of these parameters that have a direct connection with the level and speed of electron transfer from microorganism to anode and the transfer of electron in circuit, and in other words have a significant role in MFC performance is electrode surface area because it creates limitation in the number of microorganisms that can reach to anode. Electrode surface area is one of the factors on which a few studies have been conducted. Recently some researchers have tried to increase the performance of MFC to some extent by increasing coating electrodes with Nps [7]. The unique characteristics of Nps such as the increased surface to volume ratio are found in them that act in order to increasing the performance of MFC. In this study, biosynthesized silver NPs were used for modifying electrode to increase MFC performance.

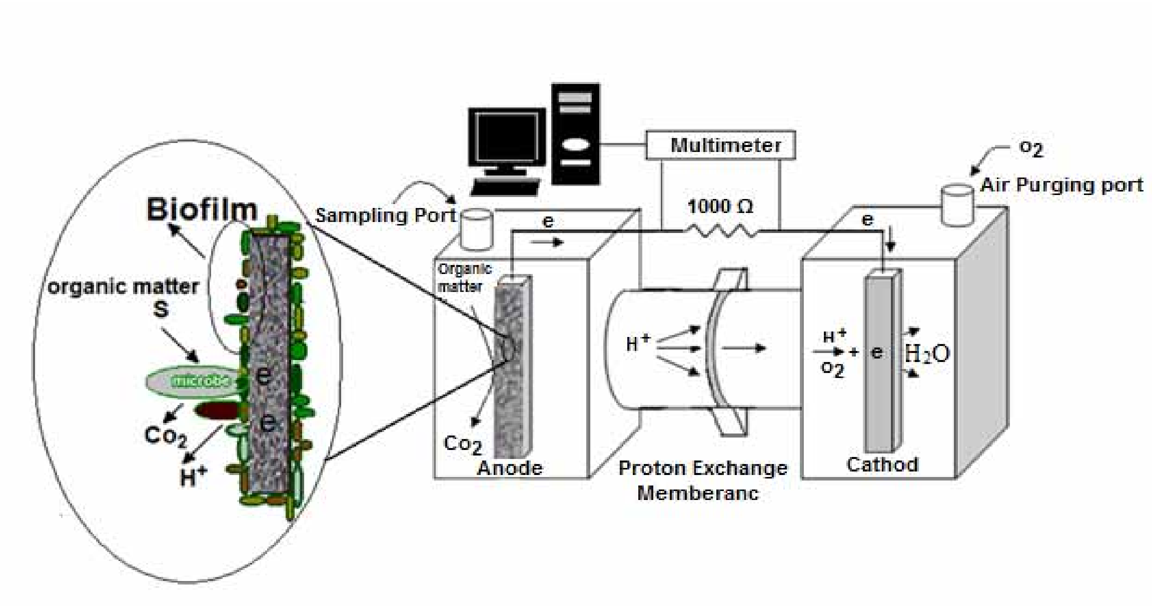

FIGURE 1
Microbial fuel cell system

MATERIALS AND METHODS

Materials. All chemicals that were used in this study such as NH_4Cl, $NaH_2PO4.H_2O$, $MnSO_4$, $Mgso_4$ and culture medium (used for growing of yeast) were obtain from Merck company, Germany. In all experiments, a graphite (10cm x 10cm) was used which was purchased from Arvin Danesh Arian Company, Iran.

Designing microbial fuel cell. For designating MFC, two cylindrical chambers that were connected by a polyethylene tube were used. For separating the content of cylindrical chambers, a proton exchange membrane (PEM) Nafion 117cs (Sigma, USA) was used. PEM pretreatment started with boiling the film in 3% H_2O_2 for 1h, washing with deionized water, 0.5 M H_2SO_4, and washing with deionized water respectively. Total volume of each chamber was 2 liter and the useful volume was 1.5 liter. The used graphite electrode was modified with biosynthesized silver Nps. In the anode chamber a small pump for circulation of substrate was used. Before performing the test, washing steps with 30% H_2O_2, 0.5M H_2SO_4, and deionized water were done exactly [8,9]. Table 1 shows the properties of PEM.

TABLE 1
Properties of proton exchange membrane

Description	Unit	Nafion 117cs
Average grain size	cm2	100
Width	μm	183
Proton conductivity	mS/cm	83

Preparation of microorganism and medium. In this study *Saccharomyces cerevisiae* PTCC 5269 was used for electricity generation in MFC. This yeast was supplied by Centre for Scientific and Industrial Research of Iran. *Saccharomyces cerevisiae* was grown in an anaerobic condition. In MFC, the medium that added to anodic chamber of MFC was contained NH_4Cl (130 mg L^{-1}), NaH2PO4.H2O (7400 mg $L^{-1)}$, $MnSO_4$ (50 $_{mg}$ L^{-1}) MgSO4 (20 mg L^{-1}) glucose (500 mg L^{-1}) and yeast extract (10 mg L^{-1}). For the cathodic chamber, all the mentioned constituents except yeast extract and glucose were used [10].

Synthesis of silver NPs. In order to perform synthesizing procedure, the clinical isolates of *Candida albicans* were cultured on Saborad Dextrose agar medium (Merck .co). 3.5 mM silver nitrate was used in order to detect and isolate yeast resistant against silver nitrate. After 24 h incubation at 37 ° C, plates that were contained of grown colonies of *Candida albicans* were isolated for next usage. In order to obtain cell mass, colonies grown were cultured in Meyer flask containing 250 ml of Saborad Dextrose broth medium (Merck .co) and also were maintained in Shaking incubator at 200 rpm for 24 h at 37 ° C. After this time, the cells were separated using centrifugation in 6000 rpm and then washed 3 times with phosphate buffer saline medium pH 7.4. Then, 5 g of wet weight yeast was removed and transferred to sterile flask containing 100 ml of 1.5 mM silver nitrate. This flask was kept in dark conditions in shaking incubator at 37 ° C. After a long time (2h); along with observed color change, biomass was maintained in shaking incubator for 48 h in order to find separated cell. In the next step, the separated cell biomass was centrifuged in 6000 rpm due to achieve the optimized condition for synthesizing of silver Nps. The yeast biomass that had ability to produce silver Nps was isolated via centrifugation in 6000 rpm and was divided into three parts for the purpose of FTIR investigation, PSA analysis and UV-vis spectroscopy [11].

Characterization of silver NPs. UV-Vis spectroscopy. Ultraviolet–visible spectroscopy was used to explore the absorption spectrum of the biosynthesized Nps. For this purpose, 50 µl of obtained solution and 50 µl of distilled water were added and analyzed with this technique at the wave length of 300-800nm [11].

FTIR investigation. FTIR spectroscopy is one of preferred spectrophotometric methods. FTIR was used due to approve accurate identification and also more exploring about features of synthesized NPs.

PSA investigation. Determining the exact size and distribution of silver Nps was also performed through PSA. In order to do this experiment, 1 ml of resulted admixed solution (the interaction of silver nitrate and cells biomass with 10 ml of distilled water) was analyzed by PSA.[12]

Modifying graphite electrode. In this study two graphite electrode types were used. Bare graphite electrode was provided through desired carbon powder and modified graphite electrode was prepared based on mixing a 3: 1 ratio of carbon powder and biosynthesized siver Nps (C) respectively. [13]

Measurements of voltage and current. Data analysis. The current produced in this study was calculated and recorded according to equation 1 and system power was calculated based on equation 2. Through dividing the values of power density and current density by the surface of electrode, the values of these two factors were calculated and recorded. The data obtained in this stage were used for plotting the polarization curve and also for the diagram of voltage change in each loading cycle. Voltage (V) changing with the external resistance in the MFC was recorded by a data acquisition system connected to a computer every 20 min. Furthermore, 10Ω, 100 Ω, 1000 Ω, 10000 Ω and 100000Ω resistances were used for indicating the relation between power density and resistance in modified electrode state and basic electro state. [14]

$I=V/R$ (1)
$P=V\times I.$ (2)

RESULT AND DISCUSSION

The characteristics of the synthesized NPs. According to the macroscopic observations, the change of color in produced biosynthesis process in the Nps indicated the existence of Nps in the reaction solution. As shown in figure 2, after adding silver nitrate salt to the yeast cell biomass, the color of the reaction mixture was changed from white to reddish-brown after 2 h. This change in color verifies the ability of *Candida albicans* in biosynthesizing of Nps.

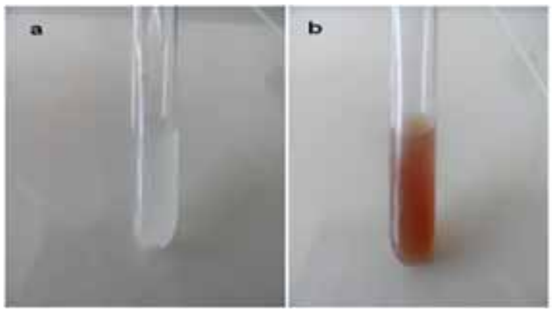

FIGURE 2
The resulted change in color after biosynthesizing of Nps

Study of UV-visible spectroscopy. Figure 3 Shows the UV- visible spectrum of synthesized silver Nps by yeast; an absorption peak found in range of 800-300 nm that was related to silver Nps and indicates shifts and surface plasmon at 420 nm. Previous researches showed that the peak absorption of silver Nps was in the range of 450-400 nm [11].

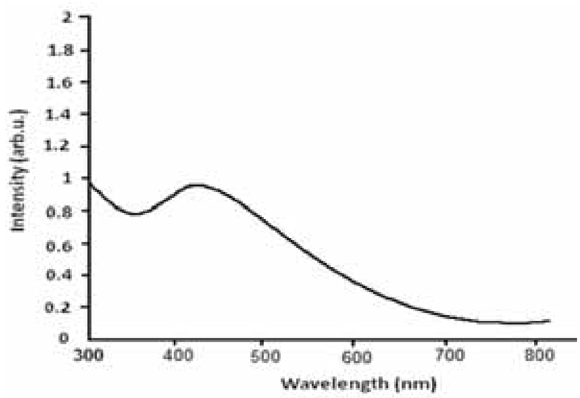

FIGURE 3
UV- visible spectrum of the synthesized silver Nps by *candida albicans*

FTIR Absorpion spectrum. Figure 4 show colloid FTIR spectrum of biosynethsized silver Nps in the 500-4000 CM^{-1} range. The created peaks, especially the peaks 1 and 2 were created in the 2500-4000 CM^{-1} range that indicate the existence of proteins around the synthesized particles; on the other hand, the mentioned created peaks indicate the preservation of the second protein stucture after interaction with silver NPs. Therefore, it can be find that the fungal proteins are reducing agents for silver nitrate solution and responsible for the synthesis of silver NPs; the recommedned mechanism for biological synthesis of silver Nps is also related to these proteins. This mechanism suggests that enzymes of a type of nitrogen reducing proteins (nitroreductases) act as reducing agents.

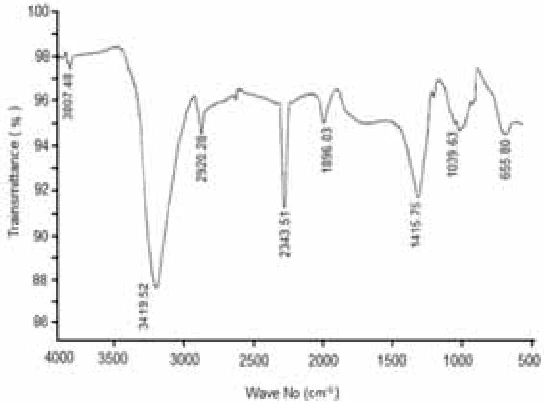

FIGURE 4
Fourier transform infrared spectroscopy of silver Nps

Determination the exact size and distribution of silver Nps via particle size analysis. Figure 5 shows the synthesized silver Nps that have average size of about 10 - 70 nm and most produced particles have a size 20 nm. This distribution of synthesized silver Nps in the nanometer range captured certain special physical and chemical properties that have many applications in various fields such as biology and medicine.

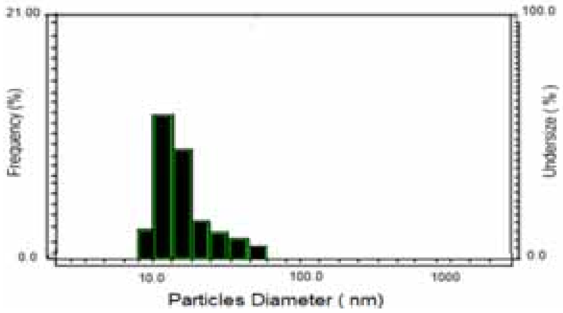

FIGURE 5
Particle size analysis of silver Nps

Figure 6 shows the SEM images of the used electrode in two conditions: before (a) and after (b) modification with biosynthesized silver Nps. Figure 6b indicates that the used electrode in this study is completely covered with biosynthesized silver NPs with special spherical morphology and average size of 10 to 70 nm. Considering the unique properties of mentioned NPs including the increased surface to volume ratio, it can be concluded that the electrode coated with biosynthesized NPs create very higher surface on the electrode for attachment, contacting and transmission of electrons.

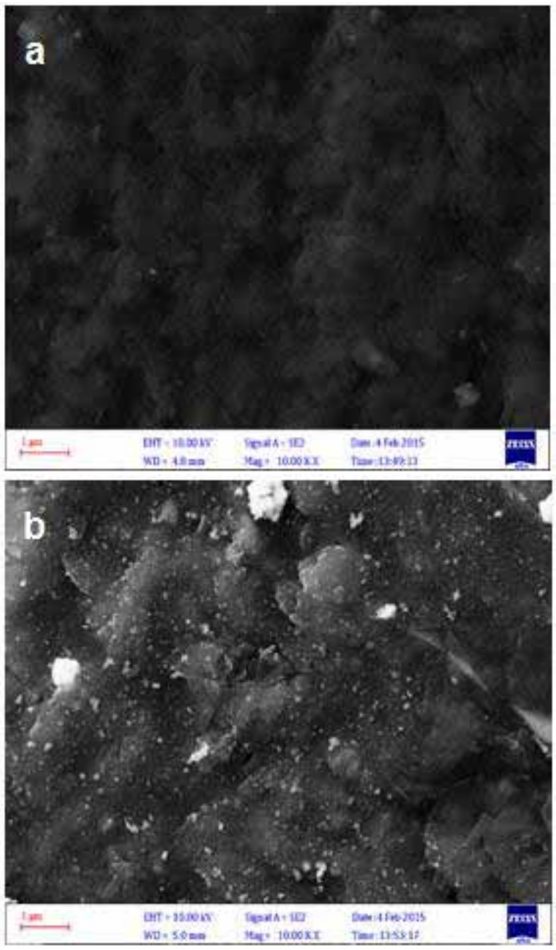

FIGURE 6
SEM images of graphite electrode; a) Before modification with biosynthesized silver Nps and b) after modification with biosynthesized silver Nps.

Figure 7 shows the energy-dispersive X-ray spectroscopy (EDX) spectrum of the modified electrode with biosynthesized silver NPs. This figure is also considered as verification for the existence of biosynthesized silver NPs and purity of them on the surface of graphite electrode.

Current and power density. The data analyzing in this study indicated that voltage for bare graphite electrode is recorded as 710 mV while for the modified graphite electrode with silver Nps it was recorded as 950 mV (figure 8). The current and power profiles for graphite electrode and modified graphite electrode by biological silver NPs are shown in figure 9. As shown in this figure the power and current density were decreased. This decrease may be due to membrane resistance, the distance between the anode and cathode or applied type of electrolyte used in the experiments. Our results showed that maximum power and current density generated for bare graphite electrode were 82 mW/m^{-3} and 1100 mA/m^{-3} respectively while the maximum generated power and current density for the modified electrode by biological silver NPs were 160 mW/m^{-3} and 1400 mA/m^{-3} respectively. Here, the obtained maximum power density and the level of voltage changes using polarization curve are considered to assessment the performance of MFC.

Efficiency of a MFC is depends on several factors such as type of electrode, the rate of electron transfer from microbial biofilm (cathod) to anode, the rate of electron transfer from anode to cathod, substrate used for biofilm formation, ohmic resistance of the electrolyte and other chemical factors [3]. Many studies have been conducted to improve the performance microbial fuel cell using metal materials [15]. Nanoparticles are useful materials that can have ameliorative impact on performance of a MFC [16]. Overall, the increasing

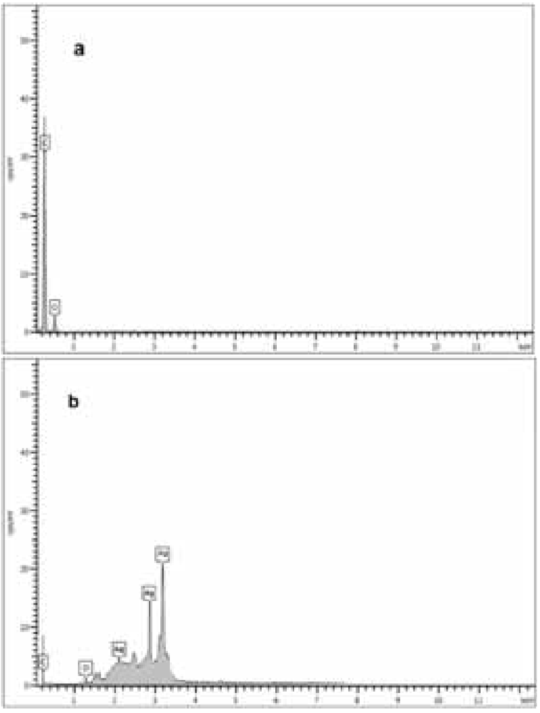

FIGURE 7
EDX spectrum. a: Basic electrode: b: Modified electrode with biosynthesized silver NPs

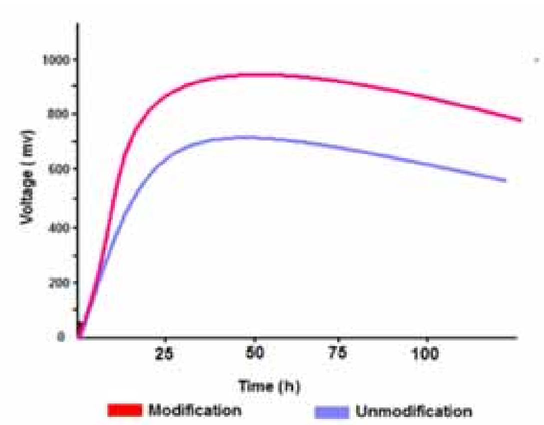

FIGURE 8
Voltage changes in designed MFC

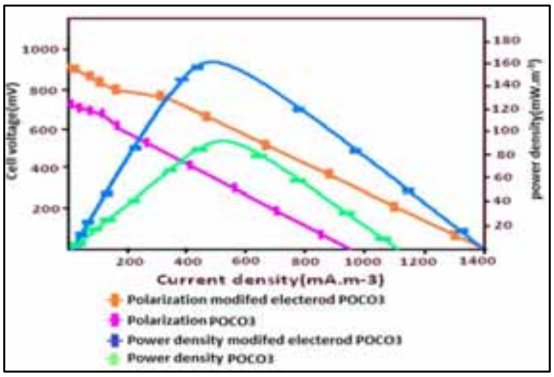

FIGURE 9
Polarization and power density in designed MFC

surface area to volume ratio that occurs gradually with the reduction of particles size results in the domination of behavior of atoms on the particle size on the behavior of the internal atoms. This phenomenon impacts the particle properties as isolated form and in interaction of materials. High surface area is a key factor in the performance of catalysts and structures of electrodes. The efficiency of chemical catalysts and electrodes can be effectively improved using this property [17].

This study has tried to improve the MFC performance by modification of electrode with biosynthesized silver Nps for the first time. These results showed the increase of efficiency of MFC with the electrode modified with silver Nps. In a study, reported output power of MFC was increased from 0.65 mW/m^{-2} to 788 mW/m^{-2} in the yeast Saccharomyces and modified electrodes with Mn^{4+} [18]. In contrast to mentioned study, our results showed that output power of MFC in the presence of Saccharomyces and modified electrode with biosynthesed silver NPs increased from 82 to 160 mW/m^{-3}. Our result showed that the electrode modified with silver Nps increases output power 2.7 times higher than bare graphite electrode. In a study, after modification graphite electrode with Mn^{4+}, the output power of MFC was increased from 0.02 mW/m^{-2} to 10.2 mW/m^{-2}. Our result showed that when graphite electrode is coated and modified by biological silver Nps, its output power is increased from 82 to 160 mW/m^{-3}. [20]. Alatraktchi et al used gold NPs with an average size of 50 to 100 nm for the assessment of MFC performance. By using modified electrode with these NPs, they concluded that the performance of MFC was significantly increased. Also, in our study the performance of MFC was significantly increased but this matter should be considered that the used nanoparticles in our study were synthesized via a biological method and their size was between 20 - 70 nm [20]. In another study, Wen et al explored the MFC performance in the presence of TiO_2 NPs [21]. The results of their research indicated that voltage, power density and current density were increased during using of the modified electrode with these

Nps. Also, in the presented study, the using of modified electrodes with biosynthesized silver Nps led to increasing the power density, current density and voltage. However, the Nps in the present study were synthesized using a biological method that can be considered as an important advantage.

CONCLUSION

Technology of biological fuel cells is one of the newest methods for electricity generation from microbial biomass. Designing of fuel cell system is considered as one of the most important and hot approaches due to achieving to related advanced technology using microbial fuel cell systems. In this study we used of microbiology, nanotechnology and electrochemistry to obtain new microbial form of electricity. Along with increasing of generated power and current density in the presence of modified graphite electrode against bare graphite electrode, it can be concluded that silver Nps provide more surface for electron transfer from anode to cathode pole.

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