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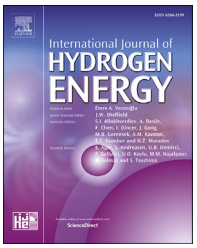

Biosynthesized FeO nanoparticles coated carbon anode for improving the performance of microbial fuel cell

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ABSTRACT

In recent, electrode coated with nanoparticles is an alternative method to enhance power output of microbial fuel cells (MFC). The utilization of nanoparticles coated electrode effects on biological application is still unidentified. In this study hydroalcoholic *Amaranthus dubius* leaf extract mediated iron oxide nanoparticles were synthesized from Ferric chloride. The prepared iron oxide nanoparticles were characterized using various analytical techniques. The antibacterial as well as the antibiofilm activity of nanoparticles and carbon paper coated with nanoparticles were investigated against isolated bacteria from distillery waste water using disc diffusion and crystal violet assay method. The effect of nanoparticles coated electrode on the performance of MFC was investigated and compared with bare electrode. The characterization results show that iron oxide nanoparticles had better physico-chemical properties. The antibacterial assay confirmed that test organism was more resistant against nanoparticles and coated electrode. The results confirmed that the power density was increased to 31% by using nanoparticles coated electrode (145.5 mW/m^2) as compared to bare electrode. Cyclic Voltammetry (CV) analysis reported that the exoelectrogensis was promoted by nanoparticles. Impedance results revealed that the anodic charge transfer resistance decreased with modified anode. The COD removal efficiency of 68.5 and 63.1% for nanoparticles coated and bare electrode. The results demonstrated that FeO nanoparticles coating enhanced the performance of MFC.

Introduction

In current epoch, the synthesis of iron oxide nanoparticles has been intensively enhanced not only for its auspicious traits, but also for numerous technological uses [1]. Iron oxide (FeO) nanoparticles (NPs) have several unique properties such as super paramagnetic behavior, biocompatibility as well as chances of chemical amendment of their surface [2]. Ascribed to its chattels, FeO NPs expediently applied in photocatalytic process, antimicrobial agent [3,4], magnetic storage media, biosensing applications [5], medical exercise such as targeted drug delivery [6], biomedical application [7].

The development of simple and biocompatible process are required for non-toxic, inexpensive NPs synthesis. Akhtar

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et al. reviewed that plant extracts have an immense potential to produce NPs [8]. Moreover, this approach has increasing; owe to economic feasible way and is easy to scale-up for production. Seabra et al. reported that biogenic synthesis of nanostructure iron compounds holds advantages of good biocompatibility, environmental stability, low cost and unique electric property, making it as a good material for biological to biomedical application [9].

In this state, Microbial fuel cell (MFC) is one of emerging-energies, acts as an auspicious technology that converts the chemical energy stored in the wastewater into electricity; simultaneously removing the pollutants by means of catalytic activity of microorganism [10]. The MFC consist of anode and cathode chamber separated by proton exchange membrane. The microorganism released electrons and protons during oxidation of organic matter in anode side. These are combined with electron acceptors in the cathode side to produce electricity [11]. Over the last ten years, the MFC performance was significantly improved by varying the parameters such as concentration, pH, electrode materials, types of electrolyte and reactor configurations [12–14]. But, enhancing power generation and developing low-cost electrode materials become a critical in MFC technology for the real time applications. However, successful resolution has not been engraved yet for the effectual electrode architecture and its modification.

Recently, advances in nanofabrication provides an unique opportunity to develop an efficient electrode materials due to the remarkable structural, electrical and chemical properties of nano-materials [15], such as Iron, Gold, activated carbon etc. [16,17]. It was reported that iron (III) oxide advantages of good biocompatibility, environmental, anodic stability and low cost material. Iron oxide has exhibited an exceptional electric traits owe to its transfer of electrons between Fe(II) and Fe(III) and higher conductivity ($\sigma = 2 \times 10^4$ S m^{-1}) than most of other metal oxides. Iron oxide coated in the anode not only enhanced the power output, but also increased the anodic capacitance and making as an excellent electrochemical capacitor. In addition, nano Fe_3O_4 is advantageous to improve the transient charge storage of anode associated with enhancement of power recital in the MFCs [17,18].

It is a great concern to study the influence of alterations in surface morphology and chemistry brought by nano-materials on performance of MFC [16,19–21]. Though, no inclusive study in MFC has been performed on the effects of NPs with different chemical composition, mechanism and morphologies. Also the utilization of NPs effects on biological applications still unidentified [22].

With this perception, FeO NPs was synthesized from hydroalcoholic *Amaranthus dubius* leaf extract. Antimicrobial as well as antibiofilm activity for NPs and microbial interaction was tested using disc diffusion and crystal violet method. The NPs was coated on carbon paper and assembled into MFC reactor as the anode to investigate and compare the performance with bare (Plain carbon paper) electrode. CV and electrochemical impedance spectroscopy (EIS) were also used to elucidate the role of NPs in anodic bioelectrochemical reactions.

Materials and methods

Chemicals utilized

The chemicals such as ferric chloride ($FeCl_3$), sodium hydroxide (NaOH), hydrochloric acid (HCl), DPPH, ethanol, crystal violet, polyvinyl alcohol (PVA, M.W. = 125,000), Dimethyl sulfoxide, potassium ferricyanide, Orthophosphoric acid, sodium hydroxide, nutrient broth and agar were obtained from Merck and Himedia India. The chemicals were used without any further purification. The distillery wastewater was collected nearby Trichy, India. The important characteristics of the wastewater were reported on earlier literature [14]. The collected wastewater was stored at 4 ± 1 °C for further application.

Biosynthesis of NPs

Amaranthus dubius leaf extract mediated NPs was synthesized using 25 mL of 1000 ppm leaf extract and 50 mL of 0.5 M $FeCl_3$. The leaf extract (pH 6.3) was added to $FeCl_3$ solution and continuously stirred with a magnetic stirrer at 37 ± 1 °C for 1 h. The solutions pH was adjusted using 0.1 N HCl and 0.1 N NaOH. The formation of NPs was confirmed by changing the solution color from brown to colorless with the black precipitate [23]. The precipitate of FeO NPs was collected and washed with absolute ethanol. The FeO NPs were dried in an oven at 70 °C for 3 h. These FeO NPs samples were stored in sealed bottles under dry conditions prior to use.

Electrode fabrication

The NPs coated electrode was prepared using carbon paper (Toray Co.), synthesized FeO NPs and polyvinyl alcohol (PVA, M.W. = 125,000) polymer binder solution by simple brush coating method. Prior to use, required amount of NPs was taken in the beaker and added deionized water; then it was kept in an ultrasonic water bath for 15 min under ambient condition to form a uniform sol. The PVA was added in the ratio of 1:5 (PVA to NPs wt/wt %) and dissolved in the ultrapure, followed by mixing for 6 h by magnetic stirring at 60 °C. Before coating these mixtures on electrode surface, it was kept for sonication to make uniform distribution of FeO throughout solution. The synthesized FeO polymer solution of 5 mg/cm^2 (based on electrode area) was coated on electrode surface and then dried for 12 h at 60 °C using vacuum drier. The topography of electrodes before and after nanocoating was visualized using microscope and hydrophilic—hydrophobic surfaces of electrode was measured by contact angle goniometer.

Characterization of NPs

Formations of NPs were confirmed by absorption spectrums measured by a Shimadzu UV-1800 spectrophotometer (Japan) over a wavelength range of 200–800 nm. The FTIR spectra of the leaf extract and NPs were recorded by Thermo Scientific™ Inc (USA)Nicolet™ iS™5 over a spectral range of 400–4000

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