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Enhancing the power generation in microbial fuel cells with effective utilization of goethite recovered from mining mud as anodic catalyst

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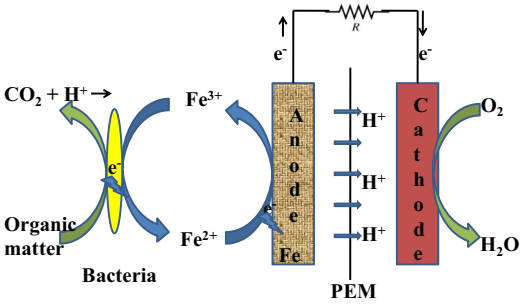
HIGHLIGHTS

- Recovery of goethite from mine mud was confirmed from material characterization.
- Recovered goethite from iron ore mine shows catalytic behavior for anodic reactions.
- MFC with treated goethite coated anode gave fivefold power compared to control MFC.
- Improved capacitance observed in MFC with treated goethite (hematite) coated anode.
- Goethite catalyst accelerates the electron transfer between anode and microbes.

GRAPHICAL ABSTRACT



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ABSTRACT

Catalytic effect of goethite recovered from iron-ore mining mud was studied in microbial fuel cells (MFCs). Characterization of material recovered from mining mud confirms the recovery of iron oxide as goethite. Heat treated goethite (550 °C) and untreated raw goethite were coated on stainless-steel anode of MFC-1 and MFC-2, respectively; whereas, unmodified stainless-steel anode was used in MFC-3 (control). Fivefold increment in power was obtained in MFC-1 (17.1 W/m^3 at 20 Ω) than MFC-3 (3.5 W/m^3). MFC with raw goethite coated anode also showed enhanced power (11 W/m^3). Higher Coulombic efficiency (34%) was achieved in MFC-1 than control MFC-3 (13%). Decrease in mass-transport losses and higher redox current during electrochemical analyses support improved electron transfer with the use of goethite on anode. Cheaper goethite coating kinetically accelerates the electron transfer between bacteria and anode, proving to be a novel approach for enhancing the electricity generation along with organic matter removal in MFC.

1. Introduction

Microbial fuel cell (MFC) is a bioelectrochemical system (BES) which can be used to treat wastewater along with simultaneous electricity generation using microbes as a biocatalyst (Logan, 2008). Anodic factors such as anodic electron transfer mechanism, material properties of electrode, microbial interaction with anode, anolyte conditions, operating conditions, etc. govern the performance of MFC. Thus, enhancing the performance of anode is a crucial aspect for scale-up of MFC technology. The main drawback associated with MFC is lower power output, primarily due to the limited electron transfer from bacteria to the anode. To enhance the power, there is a need to expend the chemical catalysts (or mediators) for anodic reactions, which are generally expensive and non-friendly to environment. Due to higher cost and chances of causing further

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pollution, use of chemically synthesized catalyst for field scale application of MFC is not a feasible solution. To solve this issue, there is a need to look for effective, economical and efficient alternative catalyst to enhance the anodic electron transfer rate.

Mining mud generated from iron ore mines can be considered as a resource; since, it contains about 60–70% of iron oxide, 10–30% of alumina; 2–20% silica; 2–10% sodium superoxide; 2–8% calcium oxide; and trace – 0.2–0.8% titanium dioxide (Paramguru et al., 2005). Higher amount of ferrous compounds present in the mud can be useful for catalytic reactions in fuel cell applications. Higher content of iron oxide compounds present in red mud can be used as inexpensive and effective anode catalysts in bioelectrochemical systems (BES). The presence of ferrous compounds could support the electron transfer in fuel cell via iron redox pathway (Kato et al., 2012). Bioelectrochemical system such as MFC can utilize this iron oxide as a catalyst to enhance extracellular electron transfer (EET) activities in the anodic chamber (Peng et al., 2013a,b, 2015).

Different forms of iron oxide (i.e. goethite, hematite, and magnetite) can serve as medium for transfer of electrons between bacteria and anode (Zhou et al., 2014). In sediment MFC, Lowy et al. (2006) found that the modification of anode with nano-crystalline magnetite (Fe_3O_4) enhanced the kinetic activity by 120% as compared to that of unmodified anode. Utilization of 5% goethite (α-FeOOH) resulted into 36% increment in power density as compared to MFC with activated carbon (AC) anode (Peng et al., 2013b). In dual chambered MFC, anode modified with indium tin oxide (ITO) and hematite (α-Fe_2O_3) nano-rods improved the power by 320% than bare anode (Ji et al., 2011). Recently, Peng et al. (2015) reported boost in exchange current density by 20% with Fe_2O_3 coated AC anode as compared to control AC anode, which was mainly due to increase in the EET in anodic chamber of MFC. The electrochemical activity and attached bacterial density of Fe-modified graphite felt anode were significantly higher than unmodified anode (Wang et al., 2013). Carbon paper anode modified with goethite nano-whiskers facilitated EET with *Shewanella loihica PV-4* strain and resulted into 60% increment in current density as compared to bare carbon paper anode (Wang et al., 2015). Zhou et al. (2014) studied effect of iron oxide amendment into freshwater sediments on performance of sediment MFC and noted that higher Fe(II) concentration in freshwater led to higher power production.

Previously, few researchers (Wang et al., 2015; Peng et al., 2013a,b) worked on ferrous oxide to enhance kinetic activity of anode in MFCs using chemically synthesized goethite catalyst, which is expensive and it may cause further pollution. However, these researchers have indicated that presence of iron oxide on anode is certainly effective for enhancing the performance of MFC. Hence, the main aim of this study was to recover goethite as a waste product from iron ore mines and utilize it as an anodic catalyst in MFC. Effect of coating of heat treated goethite on anode of MFC on the power production was evaluated and performance was compared with MFC using raw goethite coated anode and without any goethite coating on stainless steel anode. Different electrochemical techniques were adopted to facilitate the comparison.

2. Methods

2.1. Goethite recovery

Mining exploration mud was collected from iron ore mine of Noamundi, Jharkhand, India. Goethite was recovered from mining mud as per the procedure described by de Silva et al. (2011). The Fe-ions present in red mud were separated from other ions by addition of NaOH, which formed precipitate of iron hydroxide. After successive wash, iron hydroxide precipitate was dissolved in nitric acid. Precipitation of ferric nitrate solution was carried out with addition of KOH to produce ferrihydrite. The precipitate was dissolved in water to obtain ferric ion species ($Fe(OH)_4^-$) and heated to 70 °C (for 60 h), which forms crystalline goethite powder. The goethite powder was dried and sample powder was used for material characterization. For conversion of goethite to hematite, goethite powder was heated to 550 °C for 2 h in muffle furnace (Cornell and Schwertmann, 2003). To determine the specific surface area, total pore volume of goethite and treated goethite samples, nitrogen-adsorption–desorption was carried out for each sample using Brunauer, Emmett and Teller (BET) surface analyzer (SMART SORB 93, Smart Instruments Ltd., Thane, India). Before BET analysis, both raw and treated goethite samples were degassed at regeneration temperature of 120 °C for 1 h with high relative pressure (P/P_0 of N_2 = 94.93%).

2.2. Material characterization

Thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) were used to measure the quantity and rate of change in weight of the material with variation in the temperature in a controlled atmosphere, respectively. TGA measurements were conducted with a heating rate of 10 °C/min under nitrogen atmosphere at temperature ranging from 50 to 800 °C. TGA and DTG curves were recorded with a Thermo-Gravimetric and Differential Thermal Analyzer (Perkin Elmer Inc., Massachusett, USA). Energy-dispersive X-ray spectroscopy (EDX) analysis was carried out for dried goethite samples using ZEISS EVO 60 Scanning Electron Microscope (Carl ZEISS SMT, Germany) to determine the amount of different elements present in goethite samples.

During Fourier Transform Infrared Spectrometer (FTIR) analysis, the infrared (IR) spectra were recorded for goethite powder samples at room temperature in KBr pellets, using a NEXUS-870 FTIR spectrometer (Thermo Nicolet Corporation, USA), under atmospheric conditions to study interaction between nano-sized particles (Liu et al., 2013). FTIR spectrum was measured without any special thermal treatment in the transmittance mode. X-ray diffraction (XRD) is a technique that is used to identify the crystalline and amorphous materials. The phase structures of both the powdered samples were determined from X-ray diffraction (XRD) patterns, with Philips 1710 diffractometer (PW-1710, Almelo, Netherlands) using monochromatic CuKα_1 radiation at the angles 2θ = 10–100° with a scanning rate of 2° per minute. In order to measure the XRD pattern, the raw and heated goethite samples were ground at room temperature and passed through 200 mesh sieve.

2.3. Fabrication of MFC anodes

Recovered raw goethite was heated in muffle furnace at 550 °C for 2 h. The homogenous mixture of poly-vinyl alcohol (PVA) binder (at loading of 0.5 mg/cm^2) and powder form of heated goethite (at loading of 1 mg/cm^2) was coated on stainless steel (SS) wire mesh anode of MFC-1. Untreated raw goethite powder along with PVA binder was coated, in same proportions as mentioned earlier, on SS anode surface of MFC-2; whereas, goethite was not coated on SS anode of MFC-3 operated as a control to facilitate the comparison. The stainless steel wire mesh having projected surface area of 107 cm^2 was used as an anode in these MFCs.

2.4. MFC construction and operation

Three dual chambered MFCs were fabricated with a baked clayware ceramic cylinder having effective working volume of 350 mL