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Effect of anodes decoration with metal and metal oxides nanoparticles on pharmaceutically active compounds removal and power generation in microbial fuel cells

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ABSTRACT

Anodes modified with MnO_2, Pd and Fe_3O_4 nanoparticles were used in microbial fuel cells (MFCs) and their effects on pharmaceutically active compounds (PhACs) removal and power generation were investigated. Results showed that anode decoration with MnO_2, Fe_3O_4 and Pd led to different performance in removing PhACs from MFCs. Diclofenac (DCF), ibuprofen (IBF) and carbamazepine (CBZ) were more effectively removed in the MFCs with the MnO_2, Fe_3O_4 or Pd anode compared to that with the carbon black (CB) modified control anode, with a removal of 81.5%–84.0% for CBZ, 48.7%–52.6% for DCF and 18.8%–20.1% for IBF, while the corresponding parts attained with the CB anode were 71.0%–78.5% for CBZ, 28.8% for DCF and 14.6% for IBF. Iohexol (IOX) was hardly removed in all the MFCs. When common non-conductive carrier (nonwoven) was used as the anode of MFCs, PhACs were less removed compared to the MFC systems, suggesting MFCs possess specially advantages over PhACs removal. The MFCs with the Pd, MnO_2 and Fe_3O_4 anodes generated a maximum power density of 824 ± 36, 782 ± 37 and $728 \pm 33\,mW\,m^{-2}$, respectively, higher than that with the control anode ($680 \pm 28\,mW\,m^{-2}$). High-throughput sequencing results showed that the MnO_2 and Fe_3O_4 modified anodes especially enriched the exoelectrogen *Geobacter* (72.1%), while the Pd decorated anode enriched a high abundance of *Geobacter* (38.5%) and *Sphaerochaeta* (16.1%). Enhanced electron transfer, specially enriched microbial community, unique catalytic functions of the metal or metal oxides deposited on the anodes, may contribute to the enhanced performance of MFCs on power generation and PhACs removal.

1. Introduction

Pharmaceutically active compounds (PhACs), have been frequently detected in wastewater effluents, surface water and drinking water [1]. PhACs consist of pharmaceuticals, pesticides, and endocrine disrupting chemicals, etc [2]. PhACs may pose a significant threat to environmental ecosystem and human health, even at low concentrations [3]. For example, pharmaceuticals can damage endocrine systems and affect hormonal regulation in aquatic organisms and wildlife [4]. In addition, misuse and overuse of antibiotics may boost the growth of antibiotics-resistant bacteria and compromise the effectiveness of antimicrobial therapy [5]. Conventional biological treatment process generally cannot effectively remove PhACs from wastewater [6]. Therefore, it is of importance to find an alternative strategy to combat PhACs in wastewater and drinking water.

Bioelectrochemical systems (BES) are electrochemical hybrid systems which are regarded as a promising alternative for common biological wastewater treatment technology, as the energy recovered could offset partial energy consumption during the process [7]. Microbial fuel cell (MFC) is a typical BES which can remove organic pollutants via oxidization or reduction at anodes or cathodes. Recent studies have found that MFCs show the special potential to remove some PhACs possibly due to the specially enriched exoelectrogens on electrodes and unique reactor structures [8–10]. For example, degradation of atenolol, fluoxetine, norfluoxetine, trimethoprim and diphenhydramine were reported in the anode chamber of MFCs [9]. Many factors influence pollutants removal at anode electrodes, such as anode microbial composition and community, supporting materials and catalysts on electrodes, etc. The problem how to establish an effective anode electrode to enhance PhACs removal in MFCs has not been well studied up to date.

Bare carbon materials are generally used as the supporting material of anode electrodes in MFCs. Recent researchers have found that decoration of carbon material based anode with metal or metal oxides can

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change its electro-chemical behavior and influence microbial community enriched on anode [11–13]. For example, Sun et al. [13] found that anode decoration with gold increased power generation in MFCs because of the enhanced electrochemical performance of the anode and the accelerated growth of biofilm. Our previous study has found that anode decoration with biogenic nano-palladium (bio-Pd) increased power generation in MFCs due to the improved redox ability of electrode and the specially enriched exoelectrogens [11].

Palladium (Pd) is a well-known catalyst for reductive hydrodehalogenation [14]. Pd can initiate dehalogenation for chlorinated organic compounds when charged with molecular hydrogen in the presence of hydrogen donors [15]. Therefore, Pd may also possess potential to catalyze the reduction of chlorinated PhACs. Besides Pd, manganese oxide (MnO_2) and magnetite (Fe_3O_4) could also be used as the catalyst to remove PhACs [14,16,17]. MnO_2, which has a reduction potential of 1.23 V, can directly oxidize some PhACs such as triclosan, chlorophene and codeine through adsorption and promoted electron transfer [18]. Fe_3O_4 can abiotically reduce PhACs due to the presence of Fe(II) species. Fe(III) species as end-products of reduction process can be further reduced to Fe(II) by electrons from anaerobic biodegradation process in MFCs [16]. Furthermore, the Fe(III)/Fe(II) couples can act as redox mediators in MFCs to enhance pollutants removal through an electron shuttling mechanism [11]. However, the problem whether these metal or metal oxides nanoparticles can be used for anode modification to enhance PhACs removal and power generation in MFCs has not been answered and deserves further study.

In this study, anode electrodes were modified with MnO_2, Fe_3O_4 and Pd nanoparticles and applied in MFCs aimed to enhance power generation and PhACs removal. Four PhACs, i.e. diclofenac (DCF), iohexol (IOX), ibuprofen (IBF) and carbamazepine (CBZ), were selected and studied here. Cyclic voltammograms (CVs) was conducted to explore the electro-catalytic properties of the metal or metal oxide modified electrodes. High-throughput sequencing technology was used to investigate the effects of anode decoration with MnO_2, Fe_3O_4 and Pd nanoparticles on the changes of the microbial community and structure of anode biofilms. This study may help to establish a novel strategy to increase recalcitrant PhACs removal and power generation in MFCs.

2. Materials and methods

2.1. Chemicals and materials

A non-wet proofed carbon cloth was used as the anode electrode (HeSen Co. Ltd, Shanghai, China). The carbon cloth was pretreated by acetone and high temperature prior to use. Na_2PdCl_4, $FeCl_3{\cdot}6H_2O$ and $Mn(Ac)_2$ were purchased from Sinopharm Chemical Reagent Co. (Beijing, China). DCF, IOX, IBF and CBZ were purchased from Sigma-Aldrich (purity > 99%). HPLC grade acetonitrile and methanol were purchased from Mreda Technology Co. (Columbia, USA). All other reagents used in this study were of analytical grade if not noted otherwise.

2.2. Synthesis of MnO_2, Fe_3O_4 and Pd nanoparticles

Fe_3O_4 nanoparticles were synthesized according to the procedure previously described by Cao et al. [19]. $FeCl_3{\cdot}6H_2O$ and sodium dodecylbenzene sulfonate were mixed and dissolved in ethylene glycol to make Solution A. NaOH was dissolved in ethylene glycol to make Solution B. A homogeneous mixture of Solution A and Solution B was prepared through mixing under vigorous magnetic stirring and then it was transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was tightly sealed and heated at 200 °C in an oven for 90 min. After cooling to room temperature, the precipitation was rinsed with deionized water and absolute alcohol repeatedly, and then dried at 60 °C for further use.

The MnO_2 nanoparticles were prepared according to a previous publication [20]. Briefly, a $KMnO_4$ aqueous solution was added to a Mn $(Ac)_2$ aqueous solution under vigorous magnetic stirring and further sonicated for 1 h for reaction. The final product of MnO_2 was rinsed with deionized water, dried at 60 °C, and then stored at 4 °C for later use.

Pd nanoparticles were prepared using *Shewanella oneidensis* MR-1 as the reducing bacteria, which can reduce Pd^{2+} to Pd^0 on cell walls and in periplasmic spaces [21]. *S. oneidensis* MR-1 was cultured aerobically in Luria-Bertani (LB) medium at 28 °C and then collected through centrifugation at 3000*g*. Pd nanoparticles was produced by *S. oneidensis* MR-1 suspension in M9 medium, as described by Windt et al. [21]. The Pd associated biomass was burned at 500 °C for 1 h and Pd powder was obtained for later use.

2.3. Preparation of MnO_2, Fe_3O_4 and Pd modified electrodes

MnO_2, Fe_3O_4 and Pd nanoparticles were loaded to the surface of pre-treated carbon cloth (2.5 × 2.5 cm^2) using 5% Nafion (DuPont Co., USA) as the binder. In brief, the prepared MnO_2 (Fe_3O_4 or Pd) nanoparticles were mixed with carbon black powder and added by Nafion and isopropanol to make a mixed paste. The paste was then spread to each side of the pretreated carbon cloth and dried in an oven at 121 °C. The amount of MnO_2, Fe_3O_4 and Pd onto the carbon cloth electrodes was 5 mg cm^{-2}. Only carbon black modified carbon cloth was used as the control anode in MFCs. An anode electrode made of non-conductive material-nonwoven cloth was also investigated in MFCs to mimic common biofilm carrier in the bioreactor. At least three repeatable samples were prepared for each type of above electrodes and used for the following experiments.

2.4. MFC setup and operation

Dual-chamber MFCs were used for the whole experiment, which were composed of an anode chamber and a cathode chamber separated by a proton exchange membrane (PEM) (Nafion 117, DuPont Co., USA). Each chamber had a working volume of 27 mL (3 cm × 3 cm × 3 cm, length × width × height). Five different types of anode electrodes were tested in the MFCs, i.e. MnO_2 nanoparticles modified electrode (MnO_2 electrode), Fe_3O_4 nanoparticles modified electrode (Fe_3O_4 electrode), Pd nanoparticles modified electrode (Pd electrode), the control electrode with only carbon black decoration (CB electrode), and the electrode made of non-conductive nonwoven cloth (NW electrode). The cathode electrode was carbon paper loaded with Pt catalyst (0.5 mg cm^{-2}) on each side. Activated sludge collected from Yanjing wastewater treatment plant (Beijing, China) was inoculated to the anode chambers to enrich electricity generating bacteria on anode electrode. The anode chamber was filled with synthetic wastewater containing (per L, pH 7.0): CH_3COONa 1.64 g, NH_4Cl 0.31 g, KCl 0.13 g, $Na_2HPO_4{\cdot}12H_2O$ 10.32 g, $NaH_2PO_4{\cdot}2H_2O$ 3.32 g, a vitamin solution 5 mL and trace minerals mineral solution 12.5 mL [22]. The ionic strength of the anolyte and catholyte were 125 mM and 150 mM, respectively. When the MFCs with the different anode electrodes attained stable power generation, PhACs degradation in MFCs was investigated by adding DCF, IOX, IBF or CBZ (5 mg L^{-1}) to the above synthetic wastewater. The anode chambers were sparged with N_2 gas for 5 min to create anaerobic atmosphere before operation. The catholyte was 50 mM phosphate buffer solution (PBS, pH 7.4). All the MFCs ran at 28 ± 2 °C.

2.5. Measurements and calculations

The reactor voltage drop (V) across a 1000 Ω resistor connected between the cathode and the anode was measured by a data acquisition system (USB8253, RBH Co., China) and a personal computer. Current density (I_A) was calculated according to $I = V/RA$, where V is the voltage, R is the external resistor and A is the project surface area of anode.