INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2016) 1–11

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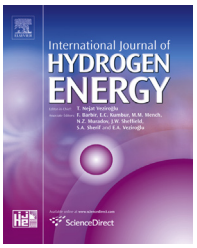

Enhanced simultaneous decolorization of azo dye and electricity generation in microbial fuel cell (MFC) with redox mediator modified anode

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ARTICLE INFO

Article history:
Received 26 July 2016
Received in revised form
22 September 2016
Accepted 29 September 2016
Available online xxx

Keywords:
Microbial fuel cell
Riboflavin
Humic acid
Azo dye
Electricity generation

ABSTRACT

Although the electrogenesis and decolorization performance can be effectively improved by adding redox mediator (RM) in MFC azo dye decolorization process, RMs are lost in vain when replacing substrates for batch run. To address this issue, RM modified anodes are prepared by electrodepositing riboflavin (RF) and humic acid (HA) on the surface of graphite felt, and air-cathode single-chamber MFCs with different modified anodes are built to decolour Congo red and generate electricity. Compared to the bare anode MFC, MFC with 0.5C RF, 0.5C HA, 1.25C RF and 2.5C HA modified anode exhibited excellent electrocatalysis activity and show 31%, 34%, 44% and 49% decrease in internal resistance along with 20%, 21%, 40% and 66% increase in maximum power density. MFCs with 2.5C HA and 1.25C RF modified anode result in high decolorization efficiency of Congo red to 86% and 75% in 16 h, which are higher than that of the bare controlled group. There are significant RM crystals on the modified anodes, and bacterial colonies on the anode surface after MFC running. The RM crystals on the modified anodes can accelerate electron transfer, which benefit both bioelectricity generation and decolorization.

Introduction

Microbial fuel cell (MFC) is a promising bioelectrochemical device which can degrade organic compounds and generate current by microbial catalysis [1,2]. MFC is expected to use for bioremediation and water treatment. It has been reported that many organic contaminants can be degraded in MFC anode, such as phenol [3], pyridine [4], 1,2-dichloroethane [5], p-nitrophenol [6] etc. Azo dye is a comment organic material in dye industry, however, it has been found to be toxic and mutagenic [7]. The special anaerobic bioelectrochemical environment in the anode of MFC creates favourable conditions for azo dyes decolorization, in which decolorization of azo dye and bioelectricity generation can be conducted simultaneously according to the theory of biological azo dyes decolorization and the operating principle of MFC [8–10]. The electrons recover from co-substrate by microbial oxidation in MFC anode are divided into two parts. One portion is

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http://dx.doi.org/10.1016/j.ijhydene.2016.09.216

transferred to azo dye molecule for reductive decolorization. The other portion is transferred to anode for electricity generation. In this process, electron transfer is the key to decolorization of azo dyes and electricity generation in MFC [11]. Therefore, enhancing the electron transfer process is an effective method to strengthen MFC performance.

To enhance the electron transfer process, some methods have been put forward. Anode modification can accelerate the electron transfer from exoelectrogen to anode, which is widely used in MFC research [12–14]. Another way is to add RM into the reactor. Researches showed that RM can effectively enhance electron transfer [15], thereby increased the reaction rate [16]. Riboflavin (RF) is an essential element for the maintenance of biological metabolism, and humic acid (HA) is widely found in nature. Both RF and HA have been considered as functional redox mediators which are widely used in bioreactors. For example, Adding 9.1 μmol L^{-1} of RF (RF: Dye = 1: 60) caused a 61% increase in the rate of mordant yellow 10 reduction by using anaerobic granular sludge [17]. The supplementation of riboflavin to anolyte can obtain higher coulombic efficiency of 7.5% because of improved electron transfer [18]. 0.5 g L^{-1} HA addition in anolyte increased 44.9% of the maximum power density and had obvious increase in coulombic efficiency [19].

The redox mediator had been proved instrumental for microbial decolorization [20–22], and in MFC systems, RM was even more frequently utilized to promote electricity generation. The peer researches had arrived at a satisfactory conclusion that MFC decolorization and electricity performance were enhanced by RM. Liu used a dual chamber MFC with thionine modified cathode to degrade methyl orange (MO), which significantly decreased the polarization resistance by over 50% and decolorization efficiency increased by over 20% [23]. And in some studies, the dye (or its intermediate) was not only the target pollutant but also as the redox mediator [24]. MFC with addition of 0.005 mM AQDS (anthraquinone -2, 6-disulphonic disodium salt), 0.005 mM RF or 1 g L^{-1} HA showed 36%, 26% and 15% increase in maximum power density respectively along with 394%, 450%, and 258% increases in decolorization efficiency of Congo red [11]. The research shows that redox mediators RF and HA can efficiently enhance the decolorization efficiency of azo dye and the electricity generation of MFCs. However, adding redox mediators into anolyte directly may cause the loss of the redox mediators, the increase of the costs, and lead to secondary pollution [25]. Accordingly, it is valuable to modify anode by fixing redox mediators on its surface. Immobilization of redox mediators on anode have been studied extensively. In Feng's study [26], the dual-chamber MFC with AQDS modified anode shows the maximum power density of 1303 mW m^{-2}, which was 13 times larger than that obtained from the MFC with an unmodified anode. Zhu [27] uses ethylenediamine modified activated carbon fibre felt as anode in MFC, which achieves a maximum power density of 1641 mW m^{-2}. Pan [28] uses a riboflavinyl-salicylaldehyde-4-aminosalicylic-1- tetracarboxylate ester (RSA) modified carbon rod anode to improve the performance of a microbial solar cell, which reaches the maximum power density of 847 mW m^{-2}, and its decolorization of azo dye (MO, OrangeII and RR) is impressive. The methods of anode modified can be summarized as Chemical synthesis [29], electrodeposition [26], and soaking [30] et al. Since the studies above have reported the advantages of modify anode, it is speculated that using RM modified anode in single chamber MFC to treat azo dye Congo red, which could achieve desirable performance since the RMs accelerates electron transfer which benefits both electricity generation and decolorization processes.

To avoid the loss of RM from the anode, we immobilize RM on the anode by electrodepositing RF and HA on the surface of the graphite felt. Then we built air-cathode single-chamber MFCs with different modified anodes (0.5 C RF, 0.5 C HA, 1.25 C RF and 2.5 C HA) to explore the benefits both decolorization of azo dye (Congo red) and electricity generation by MFC with RM modified anode in this study. Decolorization efficiency of Congo red was determined by monitoring the decrease in absorbance at the maximum wavelength of 496 nm with an UV–visible scanning spectrophotometer. The electricity generation performance of MFC was evaluated using power density and electrode polarization as electricity generation index. Cyclic voltammetry (CV) was utilized to investigate the electrocatalytic activity of RM modified anode before running, and monitor the development and electrochemical activity of biofilms after running. The charge transfer resistance in MFCs were evaluated by electrochemical impedance spectroscopy (EIS). The surface morphology of modified anode clearly observed by scanning electron microscopy (SEM) to characterize the form of the anode immobilized with RM (HA and RF), then the microorganism attached on the anode after running can be observe to roughly understand the shape of microorganism. This work may offer insights for redox mediator immobilization and anode modification, and illuminate the process of electron transfer in dye azo decolorization. Moreover, avoiding loss of RM can effectively reduce the cost of MFC operation.

Materials and methods

Preparation of anode and morphology analysis

RM modified anode was manufactured using constant voltage electrodeposition [31]. The three-electrode electrochemical cell including a working electrode (graphite felt, 5 cm × 6 cm), a reference electrode (saturated calomel electrode, 0.245 V vs. standard hydrogen electrode, 25 °C) and a counter electrode (platinum foil, 1 cm × 2 cm) were used for the electrodeposition. Before electrodeposition, graphite felt were soaked in acetone and nitric acid solution (1 N) for 12 h successively, then boiled it in deionized water for 30 min. Prepared the solutions of RF (0.02 M L^{-1}) and HA (10 g L^{-1}) respectively, then aerated nitrogen gas into the solutions for 15 min to exhaust oxygen with a magnetic stir running inside simultaneously. Afterwards, pyrrole was added into the solution and kept stirring for 15 min. Pyrrole was used for forming a polypyrrole/RM conductive polymer. Electrodeposition was conducted under 0.8 V constant voltage by using electrochemical workstation (CHI660E, China). The charge densities during electrodepositing were 0.5 C cm^{-2} and 1.25 C cm^{-2} in RF solution, 0.5 C cm^{-2} and 2.5 C cm^{-2} in HA solution. The modified anodes were named as 0.5 C RF, 1.25 C RF, 0.5 C HA and 2.5 C

Please cite this article in press as: Huang W, et al., Enhanced simultaneous decolorization of azo dye and electricity generation in microbial fuel cell (MFC) with redox mediator modified anode, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.09.216