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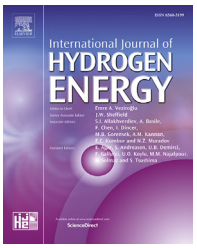

# Simultaneous degradation of P-nitroaniline and electricity generation by using a microfiltration membrane dual-chamber microbial fuel cell

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ABSTRACT

Microfiltration membrane, a potential alternative for traditional proton exchange membrane (PEM) due to its strong ability of proton transfer, cost-effectiveness, sustainability and high anti-pollution capability in microbial fuel cell (MFC). In this study, a novel MFC using bilayer microfiltration membrane as separator, inoculated sludge as biocatalyst and P-nitroaniline (PNA) as electron donor was successfully constructed to evaluate its performance. Furthermore, we also investigated the effects of initial PNA concentration, co-substrate (acetate) and cultivated microorganisms on MFC performance. Results showed that the maximum power density of 4.43, 3.05, 2.62 and 2.18 mW $m^{-2}$ was acquired with 50, 100, 150 and 300 mg $L^{-1}$ of PNA as substrate, respectively. However, with the addition of 500 mg $L^{-1}$ of acetate into reaction system contained 100 mg $L^{-1}$ of PNA, the higher power production of 6.24 mW $m^{-2}$ was obtained, which was 2.05 times higher than that using 100 mg $L^{-1}$ of PNA as the sole substrate. Meanwhile, the MFC working on cultivated microorganisms displayed a maximal power density of 7.32 mW $m^{-2}$ and a maximum PNA degradation efficiency of 54.75%. And after an electricity production cycle, the number of microbes in the anode chamber significantly increased. This study provides a promising technology for bioelectricity generation by biodegrading biorefractory pollutants in wastewater.



## Introduction

Water pollution brought by toxic refractory compounds has been attracted considerable attention particularly in some developing countries such as India, Brazil and China [1]. P-nitroaniline (PNA), one of the ramifications of nitroaniline, is a crucial material used as a precursor to produce organics, such as dyes, fuel additives and pharmaceutical chemicals [2]. This kind of aromatic ring-containing substance is considered to be

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a class of stable substances [3,4], and nitro group on the aromatic ring will further enhance the stableness of PNA, which can avoid degradation by physical or chemical ways. Besides, owing to its hematoxicity, splenotoxicity and nephrotoxicity, PNA has been classified as a major contaminant by many countries [5,6]. Therefore, techniques and methodologies for efficient PNA removal have became a hotspot in environment remediation.

Various treatment technologies have been used for PNA degradation, which include adsorption [7–9], photocatalytic degradation [10,11], Fenton oxidation [12,13], biodegradation [14]. Unfortunately, most of them have been turned out to be energy intensive, costly, non-destructive or inefficient due to high operational costs and hypervirulence of PNA in some extent. Therefore, finding a cost-effective and environmentally friendly method still remains as a challenge. Microbial fuel cell (MFC) is regard as functional devices to remove biorefractory organic compounds by making the best use of collaboration between a solid electron acceptor and metabolism microbial [15,16] and produce bioelectricity by directly converting chemical energy stored in biodegradable organic substrate into electric energy [17,18]. Thus, MFC is a promising technology for wastewater treatment, especially making best use of wastewater contained organic pollutants (such as PNA) as substrates, which can fulfil pollutant removal and electricity harvest simultaneously [19,20].

Typically, dual-chambered MFC is composed of an anode and a cathode chamber, microorganisms oxidize the organic substrate in the anode region, which is accompanied by the release of electrons and protons. The released electrons are transferred to the electrodes and then migrated to cathode through external circuit. The released protons penetrate from the anode to cathode through the internal circuit and react with electrons and oxygen, then water is formed [21,22]. The two chambers are usually segregated by traditional proton exchange membrane (PEM) (typically Nafion and Ultrex) [23–25]. However, these PEMs are expensive and approximately account for 38% of the overall cost of the construction of MFC [26]. Besides, PEM have poor ability for transferring protons from anode to cathode and further exert negative effects on MFC performance [27]. These greatly limit the application of MFC in practical wastewater treatment. Herein, more novel membranes should be explored to offset these drawbacks. According to previous literature, some novel membranes have been studied, anion exchange membrane [28], $Fe_3O_4$/PES nanocomposite membranes [29], ion permeable membrane [30]. In addition, microfiltration membrane is also considered to be a good alternative to PEM which can also transport proton and prevent dissolved oxygen entering anode chamber, and the most important is that the microfiltration membrane is quite cheap and effectively transfer protons as well as possess high anti-pollution ability. However, there are only few studies have been reported earlier.

In this study, PNA was selected as the target contaminant to study the electricity generation and PNA degradation by a novel MFC with bilayer microfiltration membranes. The property of microfiltration membrane through internal resistance and the polarization curve of MFC was tested. Furthermore, we also investigated the effects of initial PNA concentration, co-substrate (acetate) and cultivated microorganisms on MFC performance. In addition, the status of microbial growth was evaluated by comparing microorganisms quantity before and after operating the MFC one electricity production cycle. According to the real effects of MFC, some improvements are also proposed to further enhance MFC performance.

## Materials and methods

### *Inoculated sludge and synthetic wastewater*

In this study, inoculated sludge was collected from sludge thickening tank of the second wastewater treatment plant in Changsha city, China. Anaerobic activated sludge was stored at anaerobic condition before using. Refractory organic was used as the sole carbon source to cultivate anaerobic activated sludge for one month.

PNA and acetate (purchased from Beijing Chemical Company and Sinopharm Chemical Reagent Co., Ltd., respectively.) were exploited as a precursor for preparing synthetic wastewater. All of the aqueous solutions were prepared by using analytical-grade reagents and directly applied without further purification, prepared solutions were stored in the refrigerator to avoid being contaminated and not working. Ultrapure water was used to prepare and dilute all solutions.

### *MFC construction*

Scheme 1 presents a schematic illustration of the MFC constructed by plexiglass. MFC consists of two chambers separated by bilayer microfiltration membranes and each chamber's volume is 4 L with a working volume of 2 L in the practical experiments. Both anode and cathode are kryptol placed in the bottom of two chambers. The detailed information of the MFC structure display in Supplementary material. The electrodes were washed with 1 M HCl solution to remove impurity ions before the experiments. At the end of experiments, the electrodes were soaked in 1 M NaOH solution for getting rid of cells adsorbed on the surface of electrodes. Organic phase microfiltration membrane should be pretreated and stored at deionized water.

### *MFC operation*

The anode chamber was filled with 500 mL anaerobic activated sludge and 1500 mL medium solution consisted of different substrates: $NH_4Cl$ (0.31 g $L^{-1}$), KCl (0.13 g $L^{-1}$), $NaH_2PO_4$ (4.22 g $L^{-1}$), $Na_2HPO_4$ (2.75 g $L^{-1}$), a vitamin stock solution of 12.5 mL, trace metal solutions of 12.5 mL, which described in a former study literature [31]. The cathode chamber was full of medium solution contained $NaH_2PO_4 \cdot 2H_2O$ (4.22 g $L^{-1}$), $Na_2HPO_4 \cdot 12H_2O$ (2.75 g $L^{-1}$). Since both of chambers contained PBS ($NaH_2PO_4$ (4.22 g $L^{-1}$), $Na_2HPO_4$ (2.75 g $L^{-1}$)), the pH of medium solution can stay at 7.0.

A succession of experiments was conducted to evaluate the MFC performance in terms of PNA degradation and electricity generation from different substrates and cultivated microorganisms. At the beginning, MFC was operated with glucose (500 mg $L^{-1}$) as the substrate and external resistance

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