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Electricity generation using *p*-nitrophenol as substrate in microbial fuel cell

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A B S T R A C T

The cell voltage and degradation rate of *p*-nitrophenol (PNP) were monitored in a two-chambered microbial fuel cell (MFC) system. Degradation metabolites in the anode solution of MFC were analyzed by gas chromatography–mass spectrometry (GC–MS). PNP was used as substrate by the MFC that was inoculated with anaerobic sludge. The results showed that electricity output increased with the PNP concentration increased, the MFC displayed a maximum power density of 1.778 mW m^{-2} and a maximum PNP degradation rate of 64.69% when PNP was used as a sole substrate. However, the cell voltage and the PNP degradation rate with sodium acetate (402.3 mV and 95.96%) were higher than those fed with glucose (341.9 mV and 83.51%) when glucose and sodium acetate were used as a substrate, respectively. Furthermore, GC–MS analysis showed that the PNP was biodegraded completely after 142 h in the MFC. These results demonstrate that PNP can be used for electricity generation in MFC for practical applications of wastewater treatment.

1. Introduction

p-Nitrophenol (PNP) is an important nitro-aromatic compound that is used in manufacturing of dyes, pigments, explosives, fungicides, industrial solvent and organic phosphorus pesticide (Paola et al., 2003; Kuosa and Kallas, 2009). Due to its high chemical stability and toxicity to organisms, PNP is recognized as the European Economic Community list I of toxic pollutant and a priority pollutant by the US Environmental Protection Agency, and its concentration in natural water is restricted to less than 10 mg l^{-1} for environmental safety (Zhang et al., 2009).

The microbial fuel cell (MFC) is an electrochemical device that uses microorganisms as the catalysts to oxidize organic matter and convert chemical energy to electrical energy (Logan, 2005; Ieropoulos et al., 2005; Aelterman et al., 2006; Liu et al., 2009; Sun et al., 2010). Most natural substrate remains in the form of glucose, oxalate, butyrate, and other easily degradable substrates (Min and Logan, 2004; Liu et al., 2005; Wen et al., 2009). Some toxic organics can also be used as substrate in the MFC. In this study, the cell voltage and the removal of PNP in the two-chambered MFC system were investigated.

2. Materials and methods

2.1. MFC configuration

A two-chambered microbial fuel cell system was designed and constructed. Each chamber (anode or cathode chambers) was filled with 2 l of medium solution, and the two chambers were connected with a glass tube (total length, 8 cm; inner diameter, 4 cm) with two pieces of organic microporous filter membranes (pore size, 0.22 μm) in the middle of the tube. The electrodes were made of kryptol (surface area, 100 cm^2), and connected via a 1900 Ω external resistor with copper wire.

2.2. MFC operation

The MFC was started using anaerobic sludge (500 ml) in the anode chamber and phosphate buffer solution (4.22 g l^{-1} NaH_2PO_4 + 2.75 g l^{-1} Na_2HPO_4, pH, 7) in the cathode chamber at room temperature (25 ± 5 °C). The cathode chamber was continuously aerated by an aquarium membrane pump.

Substrates used in the anode chamber of MFC included PNP, PNP and glucose (G), PNP and sodium acetate (NaAC). The MFC was operated with 500 mg l^{-1} G as the fuel at the beginning. After electrical output was reached a steady state, the MFC was operated sequentially using PNP, PNP and G, PNP and NaAC as the substrates. Besides the substrates, the anodic solution also contained (per liter of deionized water): 0.31 g NH_4Cl, 0.13 g KCl, 4.97 g NaH_2PO_4, 2.75 g

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Na_2HPO_4, trace metal solution 12.5 ml, a vitamin stock solution 12.5 ml and trace metal solution 12.5 ml as described in a previous study (Lovely and Phillips, 1988).

In all operations, once the voltage outputs were below 50 mV, the substrate was replaced with a new solution for the next cycle. The voltage was measured hourly, COD and PNP concentrations of the anode chamber were analyzed daily.

2.3. Analysis and calculate

COD was analyzed by the potassium dichromate method (Huang, 1996). The concentration of PNP in the anode chamber was analyzed from the absorption intensities of species obtained spectrophotometrically (Shimadzu Kyoto, Japan) at a wavelength of 318 nm and a pH of 3–4 (Guo and Deng, 1998). GC–MS (Thermo Finnigam-TRACE GC, Polaris Q, USA) was used for identification of possible metabolites after biodegradation of PNP, the specific operating conditions refer to Chauhan (2010).

Voltage (V) was continuously measured by a digital multimeter (UNI-T 803) with a data acquisition system. Power density (P) was calculated according to $P = U^2/RA$; where U is voltage (V), R is resistance (Ω), A the surface area of electrode (m^2). Coulombic efficiency (CE) was calculated according to $CE = (\sum_{i=1}^{n} U_i t_i / RFb\Delta SV)M \times 100\%$ (Logan et al., 2006); where F is Faraday's constant (96,485 C mol^{-1} electrons), b is the number of moles of electrons produced per mole of substrate (4 mol mol^{-1}), ΔS is the substrate concentration, M is the molecular weight of the substrate (32 g mol^{-1}).

3. Results

3.1. The experimental results of MFC using different concentrations of PNP as substrate

The cell voltage, PNP degradation rate and COD removal rate in the MFC were studied when using different concentrations of PNP as a substrate. The cycle of electricity generation for cathode fed with different initial PNP concentrations is shown in Fig. 1. In this figure, the maximum cell voltage increased from 100.6 to 183.8 mV, and the maximum power density increased from 0.447 to 1.778 mW m^{-2} when the initial PNP concentration increased from 50 to 300 mg l^{-1}. Results show that the cell voltage value increased gradually first and reached to the maximum value due to sludge biological activity, and then decreased gradually till it was stable. The maximum voltage increased with the PNP concentration increase, but after the steady state, the average voltage decreased with the increase of PNP concentration.

Fig. 2 shows the PNP degradation rates and COD removal rates at different initial PNP concentrations. Over the same period, PNP degradation rate decreased from 64.69 to 33.68%, COD removal rate decreased from 62.87 to 30.67% and CE decreased from 1.128 to 0.264% when the initial PNP concentration increased from 50 to 300 mg l^{-1}. The results indicated that substrate degradation decreased with the increase of the initial PNP concentration.

3.2. The experiment results of MFC using different mixed organic matters as co-substrate

PNP can inhibit the growth of microorganisms for it is toxic, and using an easily degradable organic matter as a co-substrate is beneficial for the microbial growth. The MFC was operated using different mixed substrates with an external 1900 Ω resistor. The cycle of electricity generation for the cell fed with different initial substrate(s) (PNP 100 mg l^{-1}, PNP 100 mg l^{-1} + G 100 mg l^{-1}, PNP 100 mg l^{-1} + G 500 mg l^{-1}, PNP 100 mg l^{-1} + G 800 mg l^{-1}, PNP 100 mg l^{-1} + NaAC 500 mg l^{-1}, respectively) is shown in Fig. 3. Results show that the electricity generation was stable in the experiments. The addition of G or NaAC affected the cell voltage, which was significantly higher than that without G or NaAC, an increase from 139.2 to 341.9 mV when the G concentration increased from 0 to 800 mg l^{-1}. Moreover, when 500 mg l^{-1} NaAC was used as a co-substrate, the average voltage value was 402.3 mV and the maximum power density was 8.518 mW m^{-2}, which were significantly higher than that when 500 mg l^{-1} G was added alone.

Fig. 4 shows the results of the PNP degradation rates and COD removal rates with different co-substrate combinations. By maintaining an initial PNP concentration of 100 mg l^{-1} and G as a co-substrate, the maximum PNP degradation rate was 83.51% when G was 500 mg l^{-1}. The COD removal rates were 58.64, 74.89, 74.82 and 80.44% when 0, 100, 500, 800 mg l^{-1} G were added, respectively. But when 500 mg l^{-1} NaAC was used as a co-substrate, the

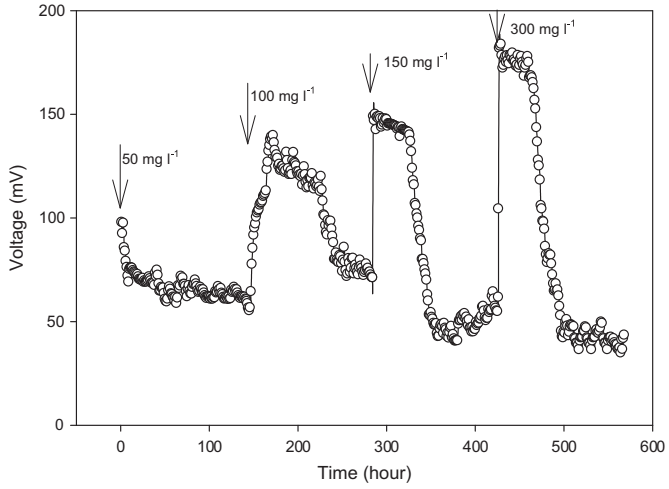

Fig. 1. Time-voltage curves of the MFC using different concentrations of PNP as substrate.

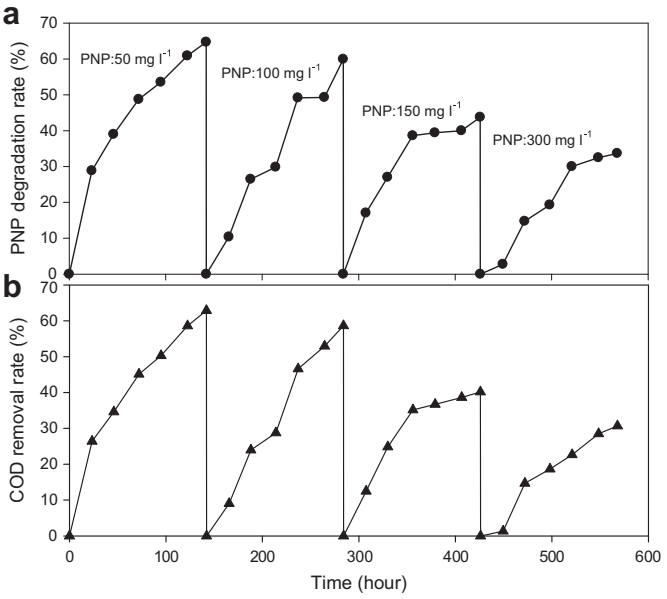

Fig. 2. PNP degradation rates (a) and COD removal rates (b) in the MFC using different concentrations of PNP as substrate.