



Short communication

Bioelectrochemical system for recalcitrant *p*-nitrophenol removal

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ABSTRACT

Bioelectrochemical system (BES) for recalcitrant *p*-nitrophenol (PNP) removal was investigated in this study. Effective removal of PNP at rates up to $9.14 \pm 0.48 \text{ mol m}^{-3} \text{ d}^{-1}$ was achieved at an energy consumption as low as $0.010 \pm 0.002 \text{ kWh mol}^{-1}$ PNP. PNP removal rate was enhanced with negative cathode potential, increased influent PNP concentration and shortened hydraulic retention time (HRT). Although the coulombic efficiencies at the anode did not exceed 40%, coulombic efficiencies for PNP removal at the cathode were above 70% at various cathode potentials. Compared with conventional anaerobic process, the cosubstrate dosage in BES was significantly reduced due to the high coulombic efficiencies at the cathode. *p*-Aminophenol (PAP) was identified as the dominant product of PNP reduction at the abiotic graphite cathode of BESs. This study demonstrated that the BES had a potential for efficient removal of nitrophenol pollutants from wastewater.

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1. Introduction

Nitrophenols in wastewater from pesticides, explosives, dyes and plasticizers industries cause serious environmental problems because they are toxic and difficult to be decomposed biologically [1]. Various methods such as advanced oxidation processes (AOPs) and aerobic biodegradation are difficult to remove nitrophenols from wastewater, due to the pronounced electron-withdrawing character of the nitro groups in their structure. In conventional anaerobic systems, nitrophenols can readily transformed to their corresponding amines, but with very low rate and high cosubstrate usage [2].

Development of BESs may be helpful for resolving the problems that arise from anaerobic reductive transformation process [3,4]. In a bioelectrochemical system (BES), the electrons transfer from an electron donor to the anode through electrochemically active bacteria. The electrons then flow through an external resistor or power user before electron acceptor reduction or hydrogen formation at the cathode [5–7]. Although BESs have been applied to remove recalcitrant pollutants such as nitrobenzene [4] and azo

dyes [3], there is still lack of great knowledge about nitrophenol removal in BESs.

The present study aims to investigate the feasibility of BESs for nitrophenols removal from wastewater, and *p*-nitrophenol (PNP) was chosen as a model. The effect of various parameters, such as cathode potential, influent PNP concentration and hydraulic retention time (HRT) on PNP removal in BESs was investigated. The possible reduction mechanism of PNP in BESs was identified and the efficiency of the BESs for recalcitrant PNP removal was also evaluated in this study.

2. Materials and methods

The setup and startup of a two-compartment BES with bioanode and abiotic cathode were described in a previous study [4]. Granular graphite without any noble metal catalysts was used as both anode and cathode material. The anode was inoculated with a microbial consortium previously enriched in BESs with acetate as the carbon source. The anode was connected to the cathode through a potentiostat (Bio-Logic Science Instruments, France) for cathode potential control. The growth medium with 320 mg L^{-1} sodium acetate as electron donor was fed to the anode at a flow rate of 540 mL d^{-1} . The cathode feed was consisted of a 50 mM phosphate buffer (pH 7) with a certain amount of PNP. After successful startup of the BES, three series of experiments were conducted to investigate the effect of cathode potential (–300 to –700 mV vs SHE), PNP influent concentration (0.72–3.60 mM) and HRT (1.3–8.5 h) on PNP removal in BESs.

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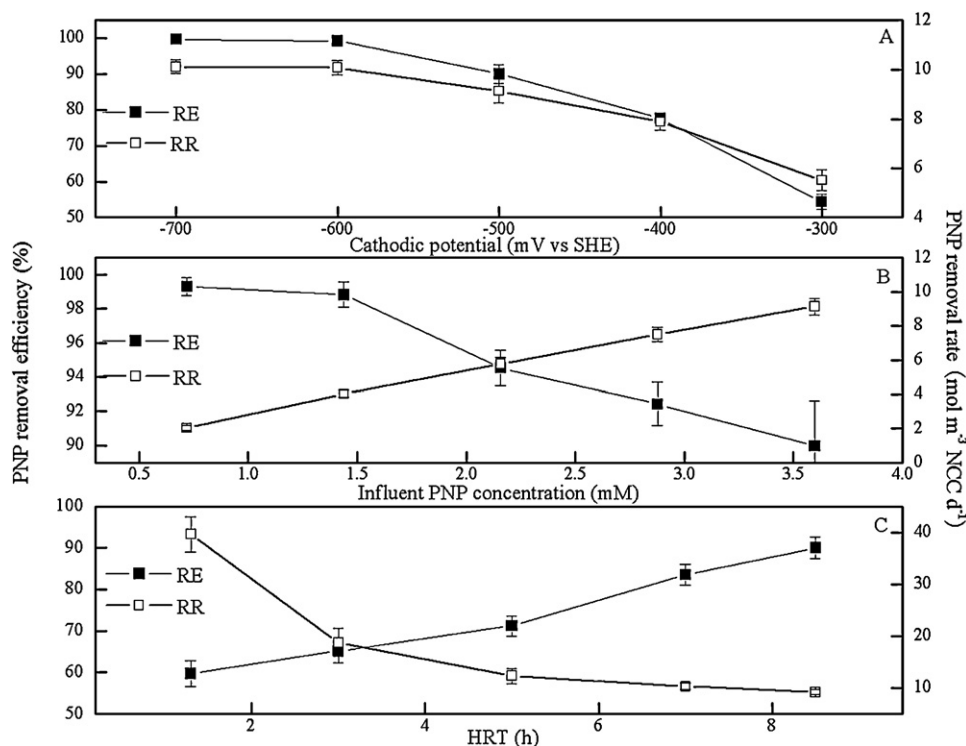


Fig. 1. Effect of (A) cathodic potential, (B) influent PNP concentration, and (C) HRT on PNP removal efficiency (RE) and rate (RR) in BES (A: influent PNP 3.60 mM, HRT 8.5 h; B: HRT 8.5 h, cathodic potential -500 mV vs SHE; C: influent PNP 3.60 mM, cathodic potential -500 mV vs SHE).

PNP and its reductive products were analyzed by high performance liquid chromatography (HPLC) using a RP18 column ($5 \mu\text{m}$, $3.9 \text{ mm} \times 150 \text{ mm}$). The mobile phase was a MeOH/H₂O 1:1 at 1 mL min^{-1} . The electrochemical monitoring and calculation was performed according to Mu et al. [4].

3. Results and discussion

3.1. Effect of various operating parameters

As cathode potential was decreased from -300 to -700 mV vs SHE (Fig. 1A), PNP removal efficiency increased from $54.35 \pm 2.15\%$ to almost 100%, and correspondingly, PNP removal rate increased from 5.52 ± 0.42 to $10.12 \pm 0.27 \text{ mol m}^{-3} \text{ NCC d}^{-1}$. A more negative cathodic electrode potential means a more reduced environment that may be more favorable to electron transfer from cathode to PNP. With the increase of influent PNP concentration from 0.72 to 3.60 mM, PNP removal efficiency decreased from $99.31 \pm 0.51\%$ to $89.98 \pm 2.63\%$, while PNP removal rate increased from 2.03 ± 0.15 to $9.14 \pm 0.48 \text{ mol m}^{-3} \text{ NCC d}^{-1}$ (Fig. 1B). When cathode HRT was increased from 1.3 to 8.5 h, PNP removal efficiency increased from $59.72 \pm 3.15\%$ to $89.98 \pm 2.63\%$. On the contrary, PNP removal rate decreased with prolonging HRT, from 39.66 ± 3.41 to $9.14 \pm 0.48 \text{ mol m}^{-3} \text{ NCC d}^{-1}$ in BES (Fig. 1C).

3.2. PNP reductive products at the cathode

Fig. 2A illustrates the UV–vis spectra of the cathode influent (PNP only) and cathode effluent. The characteristic absorbance peak of PNP at 395 nm decreased and shifted to a shorter wavelength, while simultaneously an absorbance peak at about 300 nm was formed. The new absorption spectrum has good similarity with that of *p*-aminophenol (PAP) with the characteristic peaks at 230 and 300 nm, suggesting that PAP could be the dominant product of PNP reduction at the cathode of BES. Furthermore, the peaks with

retention time of 1.5 and 9.5 min in HPLC (Fig. 2B) were identified as PAP and PNP respectively, further demonstrating that PAP was the dominant product of PNP reduction at the cathode. The product PAP exhibits the lower toxicity and higher biodegradability than PNP [8,9]. PAP could easily break down to phenol and to $\text{NH}_4^+\text{-N}$ via deamination under methanogenic conditions [9].

3.3. Coulombic efficiencies at various cathode potentials

As shown in Fig. 3, the coulombic efficiencies for PNP removal were above 70% at various cathode potentials, indicating that a majority of electrons from the cathodic electrode were used for PNP reduction. The loss of electrons could be due to hydrogen production at the cathode. However, the difference between coulombic efficiencies for PNP removal and PAP formation decreased with more negative cathodic potential, indicating that intermediate products might be formed during PNP reduction at higher cathodic potentials. At the anode, the coulombic efficiencies did not exceed 40% (varied from 29.97 ± 2.10 to 35.31 ± 2.14). In the anode, alternative processes, such as acetoclastic methanogenesis and bacterial growth were speculated to both the causes for low coulombic efficiencies. In a previous study [4], the same phenomenon was observed. Hence further investigations are necessary to better clarify the nature of these competitive anode processes and minimize their occurrence.

3.4. Implication

Although PNP can be reduced to PAP under anaerobic conditions, the reduction rate is normally low. As shown in Table 1, maximum PNP removal rate in the BES were much higher than those of conventional anaerobic systems [2,9,10], demonstrating BESs were highly efficient for PNP removal. On the contrary, cosubstrate usage in the BES was much less than those in conventional anaerobic systems, which would significantly reduce the operational cost.

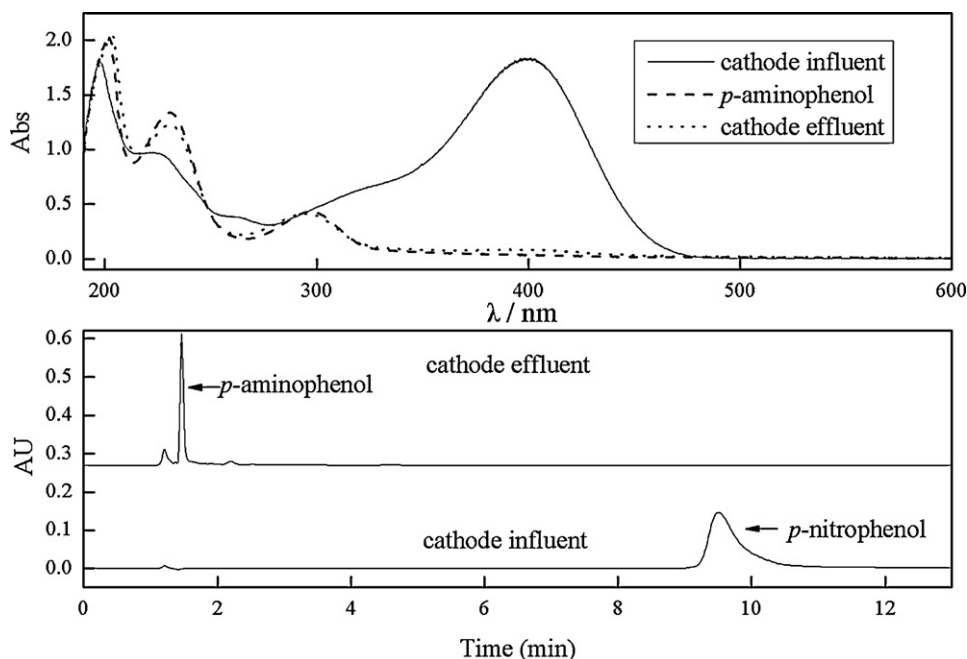


Fig. 2. Evolution of UV-vis spectra (A) and HPLC chromatogram (B) for PNP reduction in the cathode (cathodic potential -500 mV vs SHE, HRT 8.5 h, influent PNP 1.44 mM).

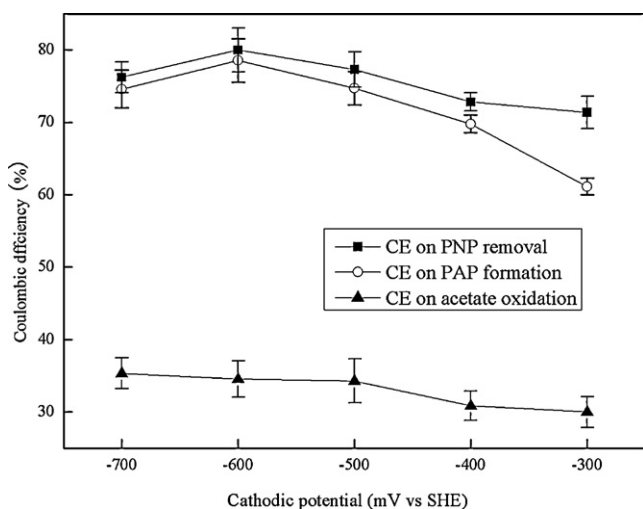


Fig. 3. Coulombic efficiency at various cathodic potentials.

The significant reduction of cosubstrate dosage in BES may be due to the high coulombic efficiencies at the cathode. Therefore, BES could be a promising alternative to the conventional anaerobic process for reductive transformation of PNP to PAP. In addition, the

Table 1
Comparison of PNP degradation in BESs with anaerobic biological methods.

Reactor	Maximum PNP removal rate (mol m ⁻³ empty bed volume d ⁻¹)	COD usage (mol COD mol ⁻¹ PNP removal)	Reference
BES ^a	9.14 ± 0.48	5.66 ± 0.15	This study
AMBR ^b	<0.07	>120	[2]
ABR ^c	<0.48	>20	[9]
UASB ^d	5.49	64	[10]

^a Cathodic potential -500 mV vs SHE.

^b Anaerobic migrating blanket reactor.

^c Anaerobic baffled reactor.

^d Upflow anaerobic sludge blanket.

BES could also be a favorable alternative for PNP removal compared with pure electrochemical systems. For instance, the energy consumption was about 2.54 kWh mol⁻¹ PNP at a removal rate of 2.35 mol m⁻³ d⁻¹ [11], and 22.72 kWh mol⁻¹ PNP at a removal rate of 15.84 mol m⁻³ d⁻¹ [8] in pure electrochemical systems. However, the energy consumption in the BES, 0.010 ± 0.002 kWh mol⁻¹ PNP at a removal rate of 9.14 ± 0.48 mol m⁻³ d⁻¹, was far lower than those in pure electrochemical systems [8,11]. These results strongly demonstrate that BES has a great potential for efficient removal of nitrophenol pollutants.

4. Conclusions

Effective removal of PNP was achieved in BESs with low energy consumption and cosubstrate usage. PAP was identified as the dominant product of PNP reduction at the cathode of BESs. The BES offers bright prospects for efficient removal of nitrophenol pollutants from wastewater.

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References

- [1] M. Kulkarni, A. Chaudhari, Biodegradation of *p*-nitrophenol by *P. putida*, Bioreour. Technol. 97 (2006) 982–988.
- [2] D.T. Sponza, Ö.S. Kuşçu, *p*-Nitrophenol removal in a sequential anaerobic migrating blanket reactor (AMBR)/aerobic completely stirred tank reactor (CSTR) system, Process Biochem. 40 (2005) 1679–1691.
- [3] Y. Mu, K. Rabaey, R.A. Rozendal, Z.G. Yuan, J. Keller, Decolourization of azo dyes in bio-electrochemical systems, Environ. Sci. Technol. 43 (2009) 5137–5143.
- [4] Y. Mu, R.A. Rozendal, K. Rabaey, J. Keller, Nitrobenzene removal in bioelectrochemical systems, Environ. Sci. Technol. 43 (2009) 8690–8695.

- [5] P.D. Kiely, R. Cusick, D.F. Call, P.A. Selembo, J.M. Regan, B.E. Logan, Anode microbial communities produced by changing from microbial fuel cell to microbial electrolysis cell operation using two different wastewaters, *Bioresour. Technol.* 102 (2011) 388–394.
- [6] D. Pant, G.V. Bogaert, L. Diels, K. Vanbroekhoven, A review of the substrates used in microbial fuel cells (MFCs) for sustainable energy production, *Bioresour. Technol.* 101 (2010) 1533–1543.
- [7] M. Villano, F. Aulenta, C. Ciucci, T. Ferri, A. Giuliano, M. Majone, Bioelectrochemical reduction of CO₂ to CH₄ via direct and indirect extracellular electron transfer by a hydrogenophilic methanogenic culture, *Bioresour. Technol.* 101 (2010) 3085–3090.
- [8] P. Jiang, J. Zhou, A. Zhang, Y. Zhong, Electrochemical degradation of *p*-nitrophenol with different processes, *J. Environ. Sci.* 22 (2010) 500–506.
- [9] Ö.S. Kuşçu, D.T. Sponza, Performance of anaerobic baffled reactor (ABR) treating synthetic wastewater containing *p*-nitrophenol, *Enzyme Microb. Technol.* 36 (2005) 888–895.
- [10] B.A. Donlon, E. Razo-Flores, G. Lettinga, J.A. Field, Continuous detoxification, transformation and degradation of nitrophenols in upflow anaerobic sludge blanket (UASB) reactors, *Biotechnol. Bioeng.* 51 (1996) 439–449.
- [11] S. Yuan, M. Tian, Y. Cui, L. Lin, X. Lu, Treatment of nitrophenols by cathode reduction and electron-Fenton methods, *J. Hazard. Mater.* B137 (2006) 573–580.