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Role of molecular structure on bioelectrochemical reduction of mononitrophenols from wastewater

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ABSTRACT

The effect of nitro-substituent on mononitrophenol (*o*-nitrophenol (ONP), *m*-nitrophenol (MNP) and *p*-nitrophenol (PNP)) reduction in a bioelectrochemical system (BES) was investigated in this study. The results show that the removal of all three nitrophenols was significantly enhanced with more negative cathode potential and shortened hydraulic retention time in the BESs. Moreover, the reduction of the three nitrophenols followed in the order of ONP > MNP > PNP in the BESs. Both quantum chemical calculation using density function theory and cyclic voltammetry analysis confirmed the reductive sequence of the three nitrophenols. In addition, the acute toxicity of nitrophenol effluent significantly decreased while its biodegradability was enhanced after treatment in the BES. Therefore, the BES technology offers bright prospects for efficient treatment of nitrophenol-containing wastewater.

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1. Introduction

Aqueous nitrophenolic effluents are relatively common industrial wastes, being produced in the manufacture of pesticides, herbicides, explosives, dyes and plasticizers, etc (Kulkarni and Chaudhari, 2006). Nitrophenols (NPs) cause serious environmental problems because they are difficult to decompose biologically. In addition, they are toxic to plants, microorganisms, animals, and humans (Karim and Gupta, 2006). Among the nitrophenols, 2-nitrophenol, 4-nitrophenol and 2,4-dinitrophenol are listed by the US Environmental Protection Agency (EPA) as priority pollutants. The US EPA recommends restricting the concentrations in natural water bodies to below 10 ng L⁻¹ (Kulkarni and Chaudhari, 2006).

Various advanced oxidation processes (AOPs), such as electrochemical oxidation (Cañizares et al., 2005), microwave assisted oxidation (Bo et al., 2006), photocatalysis (Essam et al., 2007), and Fenton and electro-Fenton oxidation (Pradhan and Gogate, 2010), have been applied for the treatment of nitrophenol-containing wastewater. However, due to the pronounced electron withdrawing character of the nitro groups, nitrophenols harbor a highly electron deficient π -electron system (Rieger et al., 2002), resulting in the difficulty in direct oxidation. In addition, most of these oxidation processes are energy and cost intensive (Gimeno et al., 2005).

Biological treatment systems may have promising applications for the removal of NP pollutants because of accumulating evidence that microorganisms are able to degrade these

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compounds (Donlon et al., 1996). Nevertheless, due to the high electron withdrawing properties of the nitro group, the electrophilic attack, which is usually the first step in aerobic biodegradation of NPs, becomes more difficult (Heiss et al., 2002). Furthermore, the conjugation of unstable nitroso and hydroxyamino intermediates results into the formation of complex azo or azoxy compounds under aerobic conditions (Sponza and Kuşçu, 2005; Karim and Gupta, 2001). Therefore, NPs are resistant to aerobic oxidative biodegradation, while they are subject to anaerobic reductive transformation (Rieger et al., 2002).

Under anaerobic conditions NPs are readily transformed to their corresponding amines (Karim and Gupta, 2001). On average, aromatic amines are 500-fold less toxic than their corresponding nitroaromatics, suggesting that anaerobic conditions can at least detoxify nitrophenolic wastewater even if not completely mineralize it (Sponza and Kuşçu, 2005; Karim and Gupta, 2001). However, for NPs, the anaerobic reductive transformation process is usually very slow and requires an electron donor (organic co-substrate or reductant) to create the necessary reductive conditions (Sponza and Kuşçu, 2005). The addition of reductant typically far exceeds the stoichiometric requirements, leading to additional costs and unwanted methane production (Mu et al., 2009b, 2009c).

Development of bioelectrochemical systems (BESs) may be helpful for resolving the problems that arise from the anaerobic reductive transformation process (Mu et al., 2009b, 2009c). In a typical BES, the electrons transferred from an electron donor (organic co-substrate or reductant) to the anode are catalyzed by an anodophilic biofilm which grows on the anodic electrode surface (Logan et al., 2006). The electrons then flow through an external resistor or power user before electron acceptor reduction at the cathode. BESs have been successfully applied to reduce nitrobenzene (Mu et al., 2009b; Wang et al., 2011), reductively dehalogenate (Aulenta et al., 2007) and decolorize azo dyes (Mu et al., 2009c) at the cathode chamber. Compared with the traditional anaerobic reductive processes, it has been demonstrated that BES technology could not only increase the reductive rate of toxic pollutants, but also significantly reduce the reductant usage (Mu et al., 2009b, 2009c).

In the effluents from nitrophenol producing industries and explosives producing industries, the coexistence of nitrophenols with different structures, such as ONP, MNP and PNP, are quite possible (Kulkarni, 2012). Although the reduction of PNP in a bioelectrochemical system was reported in our previous study (Shen et al., 2012), the relationship between the structure of NPs and their reduction activity has not yet been determined. For the reduction of nitrophenols, systematic investigations are still absent and the mechanisms involved are not fully understood.

Therefore, the present study aimed to evaluate the role of molecular structure on the bioelectrochemical reduction of mononitrophenols from wastewater. To better understand the mechanisms of reduction, the role of molecular structure was not only verified experimentally, but also via quantum chemistry calculations and cyclic voltammetry analysis. The biodegradability enhancement and toxicity reduction of nitrophenols after bioelectrochemical reduction were also evaluated.

2. Materials and methods

2.1. Reactor setup and operation

The setup and start-up of a two-compartment BES with bioanode and abiotic cathode were described in a previous study (Shen et al., 2012). A cation exchange membrane (Ultrex CMI-7000, Membrane International, USA) was placed between the anode and the cathode. The total empty volume for each compartment was about $340 \times 10^{-6} \text{ m}^3$ (Total cathodic compartment, TCC). Granular graphite without any noble metal catalysts was used as both anode and cathode material, reducing the compartment liquid volume to about $180 \times 10^{-6} \text{ m}^3$ (Net cathodic compartment, NCC; net anodic compartment, NAC). A graphite rod (5 mm diameter) was used in both the anodic and cathodic compartments to connect the electrodes to the external circuit. The cathodic half-cell potentials were measured by placing an Ag/AgCl reference electrode (assumed +0.197 V vs. SHE) in the cathode compartment of BES. The anode was connected to the cathode through a potentiostat (Bio-Logic Science Instruments, France) for cathode potential control.

The anode was inoculated with a microbial consortium previously enriched in BESs with acetate as the carbon source and continuously fed with a modified M9 medium as previously described in Shen et al. (2012). The growth medium with 500 mg L^{-1} sodium acetate as electron donor was fed to the anode at a flow rate of 1200 mL d^{-1} . Acetate was chosen as the electron donor because of its inertness toward alternative microbial conversions including fermentations and methanogenesis in the BESs (Pant et al., 2010). The cathode feed consisted of a 56 mM phosphate buffer (pH 4.5) with 100 mg L^{-1} of nitrophenol. The reason to adjust cathode feed at pH 4.5 is that nitrophenols are often produced from nitration of phenols using mixed acids, which usually results in the nitrophenols-containing wastewater in an acidic pH condition (Kulkarni, 2012).

After successful start-up, two series of experiments were conducted to investigate the effect of cathode potential (-100 to -500 mV vs. SHE) and the HRT (1–3 h) on removal of the three NPs in the BESs. In order to maintain well-mixed conditions and avoid concentration gradients and clogging of the granular matrix during continuous feeding, both the anolyte and catholyte were recirculated at an approximate rate of 50 mL min^{-1} . Each experiment was repeated at least twice at around $25 \text{ }^\circ\text{C}$.

2.2. Quantum chemical calculation

The molecular structures of the three NPs in aqueous solution were studied using DFT (Density Functional Theory) computations. The calculations were performed using the Dmol³ program mounted on the Materials Studio Modeling 6.0™ package. The quantum chemical calculations involved two steps viz. geometry optimization and energy calculations. Structures were geometrically optimized using the PBE level of theory, and then the charge densities were calculated after minimizing the energy. Double numerical basis sets, including polarization functions on all atoms (DNP), were used in the

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