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Reduction of 4-chloronitrobenzene in a bioelectrochemical reactor with biocathode at ambient temperature for a long-term operation

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ABSTRACT

In this study, the enhancement on 4-chloronitrobenzene (4-CNB) reduction was investigated in a dual-bioelectrochemical system with the cathode seeded by enriched 4-CNB degradation inoculums. We demonstrated that the biocathode had the ability to promote 4-CNB reduction and avoid more reluctant byproducts production. At room temperature, when initial 4-CNB concentration was 20 mg/L with 0.5 V external voltage, the 4-CNB removal efficiency reached 93.7%, while in the abiotic reactor and anaerobic bioreactor reduction rate were 62.9% and 88.4%, respectively. The 4-CNB was mainly converted to 4-CAN (*para*-chloroaniline). Some of the 4-CAN could be dechlorinated and form aniline (AN), which was more degradable by microorganism. The biodiversity was richer based on the result of scanning electron microscope. Results also showed that the present used reactor was feasible to simplify pollutant transformation and improve transformation efficiency compared with the single abiotic cathode and anaerobic reactor. The bioelectrochemical reactor cathode provided a promising condition for pollutants reduction.

1. Introduction

As an important industrial chemical, chloronitrobenzenes (CNBs) are widely used in the production of herbicides, insecticides, dyes, rubber and pharmacy. The CNBs are characterized by two kinds of electrophilic groups—nitro group and chlorine group which lead to the persistent biological toxicity of these compounds [1]. According to recent reports CNBs pollutants have been detected in most of the water body in China [2–5]. Especially, 4-CNB is the intermediate product in the industrial production of azo dyes and sulphur dyes. The concentration of 4-CNB could reach to 0.05–200 mg/L [6]. The existing treatment processes are physical adsorption [7], chemical reduction [8–10], Zero-valent iron (ZVI) reduction [11–13] and advanced oxidization, such as ozonation [14–16]; Fenton oxidation [17]; photocatalytic oxidation [18]. However, the physicochemical treatment methods have the disadvantage of recycling chemicals, high cost and the risk of secondary pollution. As an environmentally friendly technology, biological treatment has been also applied in the treatment of CNBs. The CNBs could be transformed or mineralize with some bacterium and fungus that were isolated [19,20]. Owning to the electron-deficient character of these compounds which cause the benzene ring is difficult to be attacked by oxygenase, anaerobic treatment is more efficient for their degradation and reduction. However, the anaerobic technology is universally inefficiency and unstable. The approaches to enhance the transformation of CNBs are on demand. In order to improve the treatment that integration of biotreatment technology and physicochemical treatment have been development [21,22].

More recently, bioelectrochemical systems (BESs) have been assessed for their ability to the treatment of these pollutants as a promising technology. Microbial fuel cell (MFC) and microbial electrolytic cell (MEC) can accomplish the purification of the wastewater and simultaneously energy harvesting (*e.g.* current or hydrogen). Some recalcitrant contaminants present in the wastewater like nitrobenzene [23], azo dyes [24], halogenated compounds [25,26] have been successfully deoxidized in the biocathode of BESs.

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As is reported in the previous research, the biocathode have the ability to deoxidize the nitro group on the benzene ring and convert it to the less toxic amino group. Moreover, the trichloroethene and iodinated X-ray contrast media (ICM) have been dehalogenated in the cathode of BESs. Both of these provide the reduction transformation feasibility of the compounds with nitro- and halogen on the benzene ring. Therefore the high-efficient reducing power of anaerobic biocathode will propose a promising way to transform halogenated nitroaromatic especially dehalogenate. Exploring the transformation path of these compounds will provide valuable insights for the subsequent treatment.

In the present study, we investigated the reduction efficiency and performance of 4-CNB in a dual BES with biocathode. The study focused on the improvement of 4-CNB reductions and the reveal of the transformation path. The reactor was operated continuously for more than 5 months using 4-CNB and glucose as substrates in the cathode chamber. The aim of the study was to offer a promising approach for the effective degradation of 4-CNB.

2. Materials and methods

2.1. Chemicals

4-CNB, 4-CAN and AN were purchased from Aladdin Chemistry Co. Ltd (Shanghai, China). Glucose ($C_6H_{12}O_6$) and sodium acetate ($C_2H_3NaO_2$) were purchased from Tianjin Yongda Chemical Reagent Co. Ltd (Tianjin, China).

2.2. BESs configuration

The BESs reactor constructed according to previous reported with a slight modification [23]. The reactor consisted of two equal-size Lexan plates (70 mm × 70 mm × 40 mm), which were separated by a cation exchange membrane (ULTREX CMI-7000, Membrane International, U.S.) with the diameter of 50 mm. The volumes of the anode and cathode chamber were 78 mL each. Carbon brush (30 mm in diameter and 40 mm in length) and graphite felt (50 mm in diameter and 10 mm in thickness) were used as the anode and cathode, respectively. Titanium wire (commercial pure titanium, TA2, 1 mm in diameter, Shanghai, China) was applied to collect current. The net volume of the anode chamber and cathode chamber were reduced to approximately 65 and 55 mL, respectively. Both of the anode and cathode were pretreated before placed in the reactor to remove the impurities that may affect the result of the experiment. The electrode potential was measured with a saturated calomel electrode (SCE) reference electrode (model-217, Shanghai, China). The external resistance was 10 Ω. The external power was supplied with a DC power supply. The whole reactor was kept strictly anaerobic during the operation.

2.3. Inoculation and operation

The BESs reactor anode was inoculated with the returned sludge (Tai Ping wastewater treatment plant in Harbin, China), which was washed and filtered before inoculation. The cathode was inoculated with the enriched inoculums, which had the ability to deoxidize 4-CNB in anaerobic condition with glucose as the co-metabolic substance.

The anode growth medium contained KCl, 0.13 g/L; $NaH_2PO_4{\cdot}2H_2O$, 2.77 g/L; $Na_2HPO_4{\cdot}12H_2O$, 11.55 g/L; NH_4Cl, 0.31 g/L, $CH_3COONa{\cdot}3H_2O$, 1 g/L, trace element 1 mL/L and Wolfe's vitamin 1 mL/L, with the PH of 7.0. The cathode of the reactor contained the same nutrient medium as that in the anode but not containing acetate. 4-CNB at a concentration of 20 mg/L and 500 mg/L glucose were mixed with the cathode growth medium and was added into the chamber. In order to keep the anaerobic environment of the chamber, nitrogen was inflated to remove oxygen in the medium before close the circuit. To avoid acetate depletion in the anode chamber, anolyte was refreshed every time when the catholyte was renewed.

Batch test was run in the stat-up and set-up operation with the external resistance of 10 Ω and DC power of 0.5 V. When the anode and cathode potentials reached −450 mV and −920 mV, respectively, it indicated that the successfully startup of the BESs reactor [27]. Open circuit reactor with enriched consortium acted as an anaerobic bioreactor and abiotic cathode BES with closed circuit were performed under identical conditions as the control experiments.

2.4. Analytics and calculations

2.4.1. Electrochemical measurements

The potential difference between anode and cathode (V) was recorded a data acquisition system (Model 2700, Keithly Instruments, USA).

Cyclic voltammetry (CV) was performed using an electrochemical workstation (model-660D, CH Instruments, USA) at 25 degrees at a scanning rate of 10 mV/s.

2.4.2. Biofilm characterization

The biofilm morphologies on the surface of the electrode were observed using a scanning electron microscope (SEM, J Helios nanolab 600i, USA). Before observation, a sample was collected and fixed overnight with paraformaldehyde and glutaraldehyde in a buffer solution (0.1 M cacodylate, pH 7.5, 4 °C), followed by washing and dehydration in water/ethanol. Samples were then coated with Au/Pt before SEM observation.

2.4.3. 4-CNB degradation

CNB and CAN were analyzed by high-performance liquid chromatography (HPLC) (Waters e2695, USA). 0.5 mL of samples were diluted with 0.9 mL methanol, then filtered through a 0.22 μm filter membrane, and analyzed with HPLC. A ZORBAXE clipse SB-C18 column (4.6 mm × 150 mm, 5 μm) (Agilent, USA) was used for reversed-phase separation and detection was spectrophotometric at 286 nm for 4-CNB and 240 nm for 4-CAN. The mobile phase was water-methanol (4/6, v/v) flowing at 0.8 mL/min. The injection volume for all samples was 10 μL

The samples collected from the cathode chamber used to detect the intermediates of 4-CNB by GS–MS (Agilent 5973/6890N, Agilent, USA). The testing condition was according to previous research [21].

3. Results

3.1. 4-CNB degradation in the BES with biocathode seeded by enriched inoculum

Concentration of 4-CNB was analyzed by HPLC during the operation time. The transformation efficiency was enhanced in the biocathode with enriched inoculums compared to that of the anaerobic bioreactor (open circuit, inoculated enriched consortium) and abiotic cathode (circuit closed, without consortium). The order of removal efficiency (RE) was as follow: biocathode (93.7%) > anaerobic bioreactor (88.4%) > abiotic cathode (62.9%) within 24 h (Fig. 1). In the open circuit reactor (sterilization), although the RE could reach 18.3% within 72 h, the reduction products were not detected in the HPLC. It indicated that the removal of 4-CNB in the open circuit control reactor was caused by the adsorption of the graphite felt.