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Efficient nitro reduction and dechlorination of 2,4-dinitrochlorobenzene through the integration of bioelectrochemical system into upflow anaerobic sludge blanket: A comprehensive study

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ABSTRACT

Bioelectrochemical system (BES) coupled upflow anaerobic sludge blanket (UASB) was developed for the removal of recalcitrant pollutants but lack of a comprehensive study. Thus in this study an integrated UASB-BES system was operated continuously for 240 d to systematically investigate the feasibility of the enhanced reduction of 2,4-dinitrochlorobenzene (DNCB), with the key operation parameters, the system stability as well as the microbial biodiversity emphasized. The results indicate that high voltage supplied had a positive effect on DNCB reduction but a negative impact for the overhigh voltage (>1.6 V). The ability to resist shock loading was strengthened in the UASB-BES system in comparison with the control UASB system. High-throughput sequencing analysis suggested that the enhanced reduction of DNCB in UASB-BES could be attributed to higher diversity and the enrichment of reduction-related species, potential electroactive species and fermentative species. Both DNCB removal and dechlorination gradually increased with the increase of operation time, indicating the improved performance of the coupled UASB-BES system. The heatmap visualized only slight differences in the microbial community during long-term operation, indicating the stability of the microbial community. The observed efficient and stable performance highlights the potential for long-term operation and full-scale application of the UASB-BES coupled system particularly for highly recalcitrant pollutants removal.

1. Introduction

As the important intermediates for the production of pharmaceuticals, explosives, dyes and pesticides, chloronitrobenzenes (ClNBs) are extensively used in the global chemical industry (Pizarro et al., 2014). The large-scale use and improper disposal of ClNBs would typically lead to the inexorable pollution of the water body and the soil. Because of its biorefractory property and biological toxicity, ClNBs have been ranked with the priority controlled contamination in many countries and need to be treated properly (Zhu et al., 2013).

Attempts to treat the ClNBs-containing wastewater via physicochemical treatment processes, such as adsorption (Guo et al., 2005), advanced reduction (Fu et al., 2014) and oxidization (Ye et al., 2010), have been made in previous studies. However, the physicochemical methods have their disadvantages of recycling chemicals, high cost and the risk of secondary pollution (Guo et al., 2015). Due to the pronounced electron-withdrawing property of the nitro and chlorine substituents on the aromatic ring, ClNBs are relatively recalcitrant in water environment and are resistant to microbial oxidative degradation (Lin et al., 2011). Fortunately, chloro- or nitro-substituents succumb to electrophilic attack more readily under the anaerobic conditions, resulting in an efficient reduction of ClNBs (Zhu et al., 2012). However, the low degradation rate and the poor system stability still limited the practical application of conventional anaerobic methods. Furthermore, the

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effluents from ClNBs-producing industries and explosives-producing industries often contain large amounts of soluble inorganic salts, typically fluctuating between 2% and 3%, which might cause deleterious impacts on biological treatment (Vallero et al., 2003; Zhang et al., 2012a).

Bioelectrochemical system (BES) has drawn much more attention in the field of bioenergy generation, wastewater treatment, synthesis of value added chemicals and desalination (ElMekawy et al., 2015; Zhang and Angelidaki, 2014; ElMekawy et al., 2014; Sharma et al., 2013), which uses electrochemically active bacteria as catalyst at the anode and/or the cathode. In particular, BES has recently possessed a tremendous potential in the reinforced transformation of persistent organic pollutants, such as nitrobenzene, azo dyes, chloramphenicol and others (Wang et al., 2011a; Liu et al., 2011; Sun et al., 2013). Compared with conventional anaerobic process, it has been demonstrated that BES could significantly increase the reductive rate of toxic pollutants. Furthermore, BES requires relatively low energy input compared to typical electrochemical process (Wang et al., 2011a). Meanwhile, microbial salinity-resistance could be improved due to electrical stimulation in the BES (Feng et al., 2015).

However, limited biomass retention in BESs, poor effluent quality and low treatment efficiency hinder the practical application of BESs as an independent wastewater treatment unit (De Vrieze et al., 2014; Tian et al., 2014). To overcome these shortages, the BES has been properly integrated into various conventional biological processes, such as bioelectrochemical membrane reactor (BEMR) (Wang et al., 2011b), upflow bio-filter circuit (UBFC) (Sukkasem et al., 2011), and BES-based sequencing batch reactor system (BES-SBR) (Wang et al., 2014). The performance in terms of pollutant removal and energy recovery was significantly improved in these BES-coupled systems. Furthermore, microbially electrocatalyzed reduction of side streams to valuable chemicals by using a mixed culture could provide us new insights into the coupling of wastewater treatment and synthesis of value added chemicals in the system (Sharma et al., 2013).

Recently, our previous study demonstrated that the coupling of BES into upflow anaerobic sludge blanket (UASB) could not only remarkably enhance *p*-nitrophenol removal but also significantly reduce organic cosubstrate consumption compared to the control UASB (Shen et al., 2014). Although the integrated system could be considered as a promising way to achieve energy-efficient wastewater treatment, there was a lack of a comprehensive study regarding the key factors influencing the system performance and system stability during long-term operation, which was of great significance for its practical application (Dong et al., 2011). Additionally, the improved performance of the BES-coupled systems could be closely related with the specific microbial community structure in it. However, limited information in terms of the microbial community structure in the BES-coupled systems is available.

Therefore, an integrated UASB-BES system was operated continuously for 240 days to facilitate the removal of 2,4-dinitrochlorobenzene (DNCB), and the objectives of this study were (1) to investigate the effect of several important factors, such as applied voltage, hydraulic retention time (HRT), and influent salinity, on the performance of the integrated system, (2) to evaluate the stability of the integrated system for a long-term operation, and (3) to reveal synergistic effect of electric field and microbial community.

2. Materials and methods

2.1. Reactor, inocula and substrate

Three lab-scale cylindrical UASB reactors were built and operated simultaneously in parallel. All of them were made of acrylic plastic with a height of 120 cm and a total volume of 7.5 L (with internal diameters of 8 and 30 cm for the bottom and upper parts of each reactor). As shown in Fig. S1, a pair of graphite felts (200 mm × 70 mm × 1 mm, Chemshine Carbon Co., China) fixed on titanium mesh (Guangzhou Baoda electrothermal Titanium Product Co. LTD., China, 200 mm × 70 mm × 1 mm, electrode distance 20 mm) were used as the anode and the cathode of the BES and were vertically inserted into the sludge bed of one UASB to form an UASB-BES coupled system. The electrodes were connected to a DC power source (PS-302D-2, Shenzhen Zhaoxin Electronic Co. LTD., China) for voltage control through Ti wires. The current was monitored by a digital multimeter (VC9807A+, VICTOR, China) with insertion of a 10 Ω resistor. The second UASB reactor was operated without electrodes inside as one control system, while another control system was same to the UASB-BES but without sludge inoculation, i.e., pure electrocatalytic system (ECS).

Both the coupled UASB-BES system and the single UASB reactor were inoculated with 1.5 L anaerobic sludge taken from an anaerobic baffled reactor to treat DNCB-containing wastewater, and the initial mixed liquid suspended solids of 8.5 g L^{-1}. The composition of synthetic wastewater was as follows: phosphate buffer (Na_2HPO_4 and KH_2PO_4, 14 mmol L^{-1}, pH 7.0), $MgSO_4{\cdot}7H_2O$ (0.2 g L^{-1}), $CaCl_2$ (0.05 g L^{-1}), DNCB (0.5 mmol L^{-1}), methanol (35 mmol L^{-1}) and SL-4 (10 mL L^{-1}). The DNCB concentration selected in this study was similar to the value in a real industrial wastewater (Shen et al., 2013). The composition of SL-4 was as described previously (Shen et al., 2009). Synthetic wastewater was continuously fed into reactor bottom by peristaltic pumps, and moreover each reactor had an external recirculation loop with an upflow velocity of 0.5 m h^{-1}. Water jackets and water cycle heating systems were used to maintain operational temperature at 35 ± 2 °C.

2.2. Reactor operation

The experimental period was divided into four phases, as was shown in Table S1. In phase I, both UASB-BES and UASB systems were operated in a batch mode for 30 days, and the intermediates of DNCB transformation were identified. Four batch assays was carried out, with each batch assay lasted for about 8 days. During the 30 days' operation, the applied voltage in the UASB-BES system gradually increased from 0 to 1.2 V. In phase II, the influent was continuously fed into the reactors at HRT of 5 d, and the effect of the applied voltage at 0, 1.2, 1.4 and 1.6 V on reactor performance was investigated in terms of DNCB removal and product formation. In phase III, the applied voltage was maintained at 1.4 V and the effect of HRT on DNCB reduction was evaluated at the HRT of 2, 3, 4, 5 d within next 70 days. In phase IV, the applied voltage and the HRT was maintained at 1.4 V and 5 d respectively, and the effect of salinity was evaluated in the range of 0%–3.0% (w/v %) with NaCl as salinity source during 70 days operation. At least three independent samples were taken and analyzed once a day in order to confirm the tendencies. The three independent analysis data were averaged and the standard deviation was calculated in this study. Each experiment lasted at least 10 days to ensure that the reactor reached a steady state, judging from the slight variation of DNCB removal efficiency, DACB and MP formation efficiency, as well as current.