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Substantial enhancement of anaerobic pyridine bio-mineralization by electrical stimulation

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ABSTRACT

Due to highly recalcitrant and toxicological nature of pyridine, the conventional anaerobic bioprocess is often limited by low removal rate and poor process stability. In this study, an electricity-assisted anaerobic system was developed in order to enhance biodegradation of pyridine from wastewater. The results showed that the performance and stability of the anaerobic reactor was remarkably improved for pyridine biodegradation with the applied direct current of 0.3 mA, where the efficiencies of pyridine and total organic carbon removal as well as NH_4^+-N formation were as high as 100.0%, 96.1 ± 1.2% and 60.1 ± 2.1% respectively. The compact biofilm due to electrical stimulation as well as the microaerobic environment in the bioanode might promote pyridine bio-mineralization in the anaerobic reactor. Moreover, the species related to pyridine biodegradation (*Desulfovibrio*, *Dokdonella*, *Hydrogenophaga*, and *Paracoccus*) were enriched in the anodic biofilm, which would be another reason for better reactor performance. This study demonstrated that electrical stimulation would be a potential alternative for the enhancement of pyridine removal from wastewater in anaerobic systems.

1. Introduction

Pyridine, a typical representative of N-heterocyclic compounds, is commonly found in wastewater discharged from the pharmaceutical, paint, rubber, insecticide, and petroleum industries, among others (Zhang et al., 2009). Pyridine has adverse impacts on human health and environmental quality due to its toxic and teratogenic nature (Mudliar et al., 2008; Zhang et al., 2009). Hence, there is an urgent need to develop effective and economically feasible methods to remove pyridine from wastewater.

Various technologies have been developed for the removal of pyridine from wastewater. Physicochemical methods such as physical adsorption (Mohan et al., 2004), photo-catalytic oxidation (Zhang et al., 2014), and microwave oxidation (Zalat and Elsayed, 2013) have different disadvantages including chemical recycling, high costs, and high energy consumption. Biological methods for pyridine degradation, which are both environmentally friendly and cost effective (Wen et al., 2013), should be able to overcome the various deficiencies of physicochemical methods. Pyridine biodegradation under aerobic conditions has been extensively reported in previous studies (Bai et al., 2009; Lin et al., 2010; Liu et al., 2015b), but this process not only requires significant aeration expenses but also could result in the nauseating odor. Therefore, pyridine biodegradation under anaerobic conditions has attracted increasing interest in recent years (Shen et al., 2015). Unfortunately, due to highly recalcitrant and toxicological nature of pyridine, the conventional anaerobic bioprocess is often limited by low removal rate and poor process stability. As a consequence, it is an imperative but also a challenging task to seek an improved operational scheme to achieve effective pyridine degradation under anaerobic conditions.

Recently the electricity-stimulated anaerobic system for the reinforced transformation of several persistent organic pollutants, such as nitrobenzene, azo dyes, and chloramphenicol, has been demonstrated (Wang et al., 2011; Liu et al., 2011; Sun et al., 2013). In

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such an approach, an electrode system is usually adopted instead of chemicals as a cathodic electron donor or an anodic electron sink (Yu et al., 2016). Compared with conventional anaerobic system itself, it has been proved that the electricity assisted anaerobic process could effectively stimulate microbial metabolism including growth and activity, and enhance the biodegradation efficiency of microorganisms, depending on the direct current applied (Li et al., 2010; Ailijiang et al., 2016). Moreover, electrical stimulation has been shown to have a direct effect on microbial community evolution, leading to adaptation to unique environments and the development of specific functions (Zhang et al., 2012). For example, analysis of microbial communities indicated that bacteria species used for polycyclic aromatic hydrocarbons and phenolic biodegradation were enriched when a direct current was applied (Ailijiang et al., 2016). It was also observed that phenol removal efficiency increased by 33% when a direct current was applied on a biofilm reactor with propylene packing as carrier (Li et al., 2006).

The present study aimed at investigating the feasibility of electrical stimulation for enhanced biodegradation of pyridine in anaerobic systems. An electricity-assisted anaerobic system was developed and continuously operated for 170 days. The specific objectives of this study included: (1) to investigate the effects of various key factors on the reactor performance; (2) to explore the characteristics and interplay of the micro-environment in the bio-anode using microelectrode measurements; and (3) to elucidate the variation of microbial community in the anaerobic system with electrical stimulation.

2. Materials and methods

2.1. Reactor, inocula and substrate

A tubular anaerobic reactor was constructed from acrylic plastic with dimensions of 8 cm (diameter) × 10 cm (width). Its effective volume was 500 mL. A pair of graphite felts (GF) (φ = 6 cm, electrode distance 3 cm, Chemshine Carbon Co., China) was packed into the anaerobic reactor to form an electric-biological reactor, as shown in Fig. S1 of supporting information (SI). An Ag/AgCl reference electrode (+0.197 V vs standard hydrogen electrode, SHE) was inserted into the system for potential measurement. The electrodes were connected to a regulated DC power source (PS-302D-2, Shenzhen Zhaoxin Electronic Co. LTD., China); the current was controlled through titanium wires. The output voltage of the electricity assisted anaerobic system was recorded with a digital multimeter (VC9807At, VICTOR, China).

Anaerobic reactor was inoculated with 0.2 L of sludge taken from a 3.4 L lab-scale bioreactor treating pyridine-containing wastewater. The initial concentration of mixed liquor suspended solids was 4.5 g L^{-1}. The composition of synthetic wastewater was as follows: phosphate buffer (7 mmol L^{-1}, pH = 7.0), $MgSO_4 \cdot 7H_2O$ (0.2 g L^{-1}), $CaCl_2$ (0.05 g L^{-1}), and trace element solution SL-4 (1 mL L^{-1}) according to a previous study (Shen et al., 2009). The synthetic wastewater was continuously fed into the bottom of anaerobic reactor with peristaltic pumps, and it passed through the anode and then the cathode zones. Pyridine was dosed into anaerobic reactor as the sole carbon source at the desired concentrations. Pyridine with analytical grade (purity > 99.9%) was purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). The temperature of anaerobic reactor was kept at 35 ± 2 °C in a water bath.

2.2. Reactor operation

The experimental period was divided into five phases and the experimental conditions of each phase are summarized in Table S1 of SI. All of experiments were conducted with a continuous mode in the anaerobic reactor. In phase I of the start-up period, the anaerobic reactor was inoculated and continuously fed with synthetic wastewater containing 100 mg L^{-1} pyridine, resulting in a hydraulic retention time (HRT) of 72 h. The circuit was open and thus the anaerobic reactor was considered as a control system. Once pyridine was completely degraded in the reactor, its influent concentration was gradually increased to 300 mg L^{-1} in order to evaluate reactor performance at high pyridine loading rates. When reactor performance reached to a steady state judged from stable pyridine and total organic carbon (TOC) removal as well as NH_4^+-N formation, the circuit was closed and the current was gradually increased to 0.3 mA with continuously feeding synthetic wastewater containing 300 mg L^{-1} pyridine into the anaerobic reactor, resulting in the biofilm formation on the anode and cathode in the following 18 days. In phase II, the effect of influent pyridine concentration in a range of 300–600 mg L^{-1} on reactor performance was investigated in terms of pyridine removal and NH_4^+-N formation with a controlled current of 0.3 mA and HRT of 72 h. The anaerobic reactor was run for at least 6 days at each pyridine concentration to reach a stable performance. The control experiments were also conducted in an abiotic electrolysis system at HRT of 72 h with influent pyridine concentration of 300 mg L^{-1} and the applied direct current of 0.3 mA. In phase III, the impact of the applied current in a range of 0–0.4 mA on pyridine removal were evaluated with influent pyridine concentration at 500 mg L^{-1} within the following 30 days. In phase IV, the role of HRT on pyridine oxidation were evaluated at an applied current of 0.3 mA. In phase V, the applied current and HRT were maintained at 0.3 mA and 36 h respectively, and the influence of acetate dosage was evaluated in the range of 0–15.8 mM.

2.3. Analytic methods

Before the analysis, water samples taken from the reactor were immediately filtered through a 0.22 μm membrane. Pyridine was identified and quantified using High Performance Liquid Chromatography (LC-20, Shimadzu, Japan) with an authentic standard. The mobile phase was water-methanol (3:7, v/v) flowing at a flow rate of 1.0 mL min^{-1}, and the column temperature was 35 °C. The injection volume for all samples was 10 μL. An Inerstil ODS-SP C18 (4.6 mm × 250 mm, 5 μm) column (Shimadzu, Japan) was used for reversed-phase separation, and the detection was spectrophotometric at 254 nm. NH_4^+-N was analyzed according to the Chinese National Environmental Protection Agency (NEPA) standard methods (1997). TOC concentration of the samples was measured using a TOC analyzer (vario TOC, Elementar, Germany). Acetate concentration was determined through an ion chromatograph (ICS-2100, DIONEX, UK) using an Ion Pac® As11-HC (4 mm × 250 mm) column and a suppressed conductivity detector. Scanning electron microscopy (SEM) observation and electrochemical monitoring were carried out according to Ho et al. (2009) and Shen et al. (2012). Both oxygen concentration and pH value profiles in the anodic biofilm were measured using a microelectrode automation system (PA2000, Unisense, Denmark).

Pyridine and TOC removal efficiencies were determined according to Shen et al. (2015), and ammonia formation efficiency (FE_{NH4+-N}) was calculated from the following equation:

$$FE_{NH_4^+-N} = \frac{C_{NH_4^+-N}}{C_{Pyridine}} \times 100$$

where C_{NH4-N}^{+} is the effluent NH_4^+-N concentration, mM; $C_{Pyridine}$ is the influent pyridine concentration, mM.

Average and standard deviation was calculated using Excel.