Biochemical Engineering Journal 125 (2017) 151–160

Contents lists available at ScienceDirect

Biochemical Engineering Journal

journal homepage: www.elsevier.com/locate/bej

Regular article

Biocathode denitrification of coke wastewater effluent from an industrial aeration tank: Effect of long-term adaptation

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ARTICLE INFO

Article history:
Received 10 March 2017
Received in revised form 5 May 2017
Accepted 30 May 2017
Available online 7 June 2017

Keywords:
Autotrophic denitrification
Bioelectrochemical system
Biocathode
Coke wastewater treatment
Thiobacillus

ABSTRACT

Despite recent advances in the development of autotrophic denitrification, wherein the electrode is used directly as the electron donor (known as biocathode denitrification), very little attention has been given to this approach for removal of nitrate in real industrial wastewater. This study shows that a bioelectrochemical reactor poised at −0.50 V (vs. a saturated calomel electrode (SCE)) achieved successful nitrate removal from coke wastewater effluent (CWE) sampled from an industrial aeration tank. The results show that direct exposure to CWE initially led to dramatic inhibitory effects, as evidenced by the observed lack of apparent cathodic current and small variations in the concentration of NO_3^-–N. However, long-term adaptation of the biocathode to the CWE remarkably increased the rate of dinitrification, from 2.35 (Cycle 1) to 4.93 (Cycle 3), 14.4 (Cycle 7) and 16.5 mg NO_3^-–N L^{-1} d^{-1} (Cycle 10). Both confocal laser scanning microscopy (CLSM) and electrochemical impedance spectrometry (EIS) characterizations provided evidence that long-term adaptation can induce recovery of active cells and promote electron transfer between the bacteria and the cathode. Analysis of bacterial structures suggests that cathode-driven autotrophic denitrifiers represented by *Thiobacillus* play an important role in nitrate reduction.

1. Introduction

Nitrate, as a final product of aerobic ammonium oxidation, is commonly found in effluent from aeration tanks used in the treatment of ammonium-laden wastewaters discharged from important industrial processes such as coke production, petrochemical and fertilizer manufacturing, petroleum refinement and landfill leachate. For example, the present authors previously proposed and designed a full-scale biological system consisting of anaerobic–aerobic–aerobic processes that have been successfully implemented in a coke wastewater treatment plant (Shaoguan Steel, Company, Guangdong Province of China). After ten years of stable operation, the average chemical oxygen demand (COD) concentration and ammonium concentration in the biological effluent were below 80 and 0.5 mg L^{-1}, respectively, with removal efficiency of 97% and 99%; however, this effluent still contains an average NO_3^-–N concentration of over 40 mg L^{-1} [1,2]. Further conversion of nitrate into harmless nitrogen gas is strongly desired before effluent is released into the water system, as nitrate is toxic to aquatic animals and can contribute to human health problems [3].

In general, conversion of nitrate to nitrogen by cost-effective biological denitrification is preferred over physicochemical methods such as ion exchange, reverse osmosis and activated carbon adsorption [4]. While heterotrophic denitrification is a well-established technology, it relies heavily on external organic carbon for the proliferation of heterotrophic microbes. The effluent from coke wastewater, however, lacks sufficient organics to function as electron donors for heterotrophic denitrification. Thus, autotrophic denitrification is a more attractive solution because organic carbon is not necessary [5–7]. Autotrophic denitrification, which uses the electrode directly as the electron donor (known as the process of biocathode denitrification) [8–12] in the bioelectrochemical system, has received considerable attention since the first report of nitrate reduction via *Geobacter* species [8]. This is because the controlled delivery of electrons via biocathode denitrification offers advantages such as easy operation, lower capital costs, and less sludge production. However, investigation of biocathode denitrification is still in its infancy, and most of the relevant studies have been performed with artificial nitrate-containing wastewater [9,12–14].

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http://dx.doi.org/10.1016/j.bej.2017.05.022
1369-703X/

Previous efforts have been made to elucidate the bacterial communities responsible for autotrophic denitrification in bioelectrochemical systems. Electrochemically active denitrifiers such as *Thiobacillus denitrificans* [15–17] *Paracoccus denitrificans* [18,19] and *Alicycliphilus denitrificans* [20] have been identified in the cathode biofilm in high abundances. However, little is known about whether these bacteria are capable of surviving and multiplying when exposed to complex industrial wastewater or how the microbial community varies upon long-term adaption to real wastewater laden with nitrate. To fill this gap, this study investigates the feasibility of using biocathode denitrification with nitrate-containing effluent from an industrial aeration tank treating coke wastewater, evaluates whether feeding with real wastewater impedes the denitrification process, and examines the variation in the bacterial communities resulting from long-term adaption. A bioelectrochemical reactor (BER) was constructed with its cathode poised at a potential of −0.50 V and its cathode chamber was fed with real coke wastewater containing nitrate. For comparison, artificial wastewater and O_3-treated coke wastewater effluent were also tested in the BERs.

2. Materials and methods

2.1. BER setup and operation

The BER used in this study was similar to that described previously [2,18,21]. Fig. 1 shows a schematic diagram of the BER for biocathode denitrification. It contained two 250-mL chambers separated by a cation-exchange membrane (Zhejiang Qianqiu Group Co., Ltd. China). The electrode material used in both chambers was bare graphite felt (7.0 cm × 4.0 cm × 0.5 cm) with a Ti wire (0.6 mm in diameter) inserted for the external circuit connection. To enlarge the cathode surface area, conductive graphite granules (3–5 mm in diameter) (Beijing Sanye Co. Ltd, China) were packed into the cathode chamber in direct contact with the graphite felt. Prior to use, the graphite granules were cleaned for 24 h in 37% HCl solution, followed by thorough rinsing in deionized (DI) water and drying at 100 °C overnight. The effective liquid-phase volume at the cathode was 160 mL. A three-electrode system was used to control the potential poised to the cathode by using a CHI1030 potentiostat (Shanghai CH Instrument Company, China). A cathode, anode and saturated calomel electrode (SCE) were placed into the cathode chamber as the working electrode, counter electrode and reference electrode, respectively. All potentials reported in this study refer to the SCE, unless otherwise stated. The cathode potential was set to −0.50 V, as the potential should be low enough to drive bacterial growth and/or metabolism and high enough to prevent water electrolysis. Similar cathode potentials have been used in previous studies of biocathode denitrification [8,17].

The mixed culture used for the enrichment of denitrifiers in the cathode was the supernatant taken from the sludge-based reactor, which had acclimated for more than a year using sulfur as the electron donor and perchlorate/nitrate as the electron acceptor. The acclimation procedures and the components of the basal medium were described previously [18]. The basal medium was composed of 0.41 g L^{-1} NH_4HCO_3, 0.25 g L^{-1} K_2HPO_4, 2.70 g L^{-1} $NaHCO_3$,

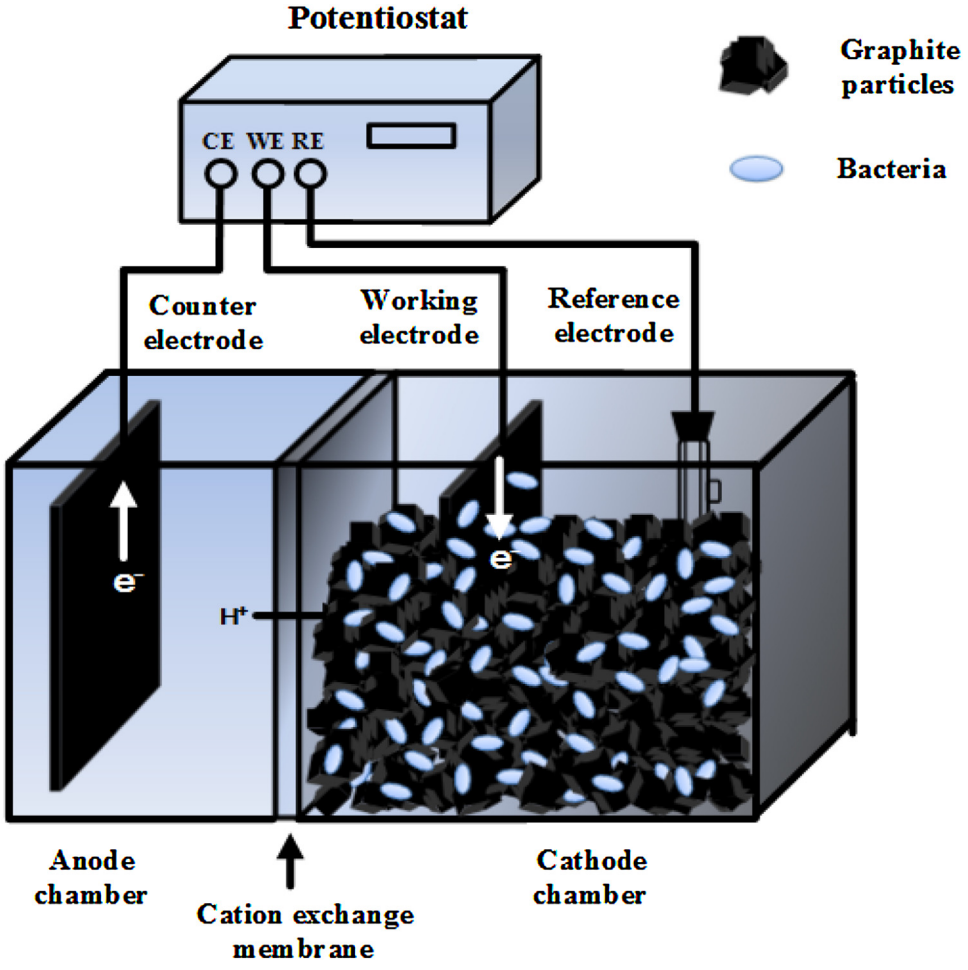

Fig. 1. Schematic diagram of the BER for biocathode denitrification.