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Short communication

Ion-exchange membrane bioelectrochemical reactor for removal of nitrate in the biological effluent from a coking wastewater treatment plant

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ABSTRACT

Bioelectrochemical reduction of nitrate using an electrode (i.e., cathode) as the electron donor represents a promising method for denitrification; however, this process suffers from the problem of being applied for treating real wastewater, because the cathodic bacteria are susceptible to poisoning by other components in the wastewater. Here we reported the concept of an ion-exchange membrane bioelectrochemical reactor (IEMBER) that integrates the transport of nitrate from a wastewater chamber through an anion-exchange membrane (AEM) with its bioelectrochemical reduction in a separate cathode chamber. Successful removal of nitrate in the biological effluent from a coking wastewater treatment plant was achieved, in good agreement with the obvious cathodic current observed in the IEMBER when its cathode was poised at a potential of −0.50 V (vs. SCE). The AEM plays a crucial role in preventing the residuals in the wastewater chamber to enter the cathode chamber, thus avoiding their potential toxicity to the denitrifying bacteria.

1. Introduction

Coking wastewater is a typical industrial wastewater in China, with a discharge volume about 2.85×10^8 m^3 per year [1]. It has been considered to be very toxic wastewater composed of complex organic and inorganic contaminants [2–4]. The core biological system consisting of anaerobic–aerobic–aerobic unit, as we proposed and designed, has been successfully implanted in the coking wastewater treatment plant (Shaogang, Guangdong Province of China) that has an average treatment capacity of 2000 m^3 per day [1,2]. After being stably operated over 8 years, the average chemical oxygen demand (COD) concentration and ammonium concentration in the biological effluent were below 80 and 4.5 mg L^{-1}, respectively. Nevertheless, this effluent contained an average nitrate concentration of 70 ± 10 mg L^{-1}, which cannot meet the requirement of total nitrogen (TN) limit from the National Discharge Standard in China. The most commonly used technology to remove TN is via the recycle of nitrified effluent to the anaerobic process where the denitrification occurs by the denitrifying bacteria; however, it substantially increases the operation cost due to the energy requirement of pumping, the increase in hydraulic retention time and/or the possible addition of external inorganic carbon source. Direct electrochemical reduction of nitrate has also been extensively studied, but this reaction relies on the noble metal like rhodium and palladium and/or heavy metal like copper as the electrocatalysts [5,6]. Here, we proposed a potentially beneficial alternative that uses the electrode as the electron donor for microbial reduction of nitrate, avoiding the continuous addition of a chemical electron donor and the use of metal electrocatalysts.

Although several previous studies [7–11] have demonstrated the concept of autotrophic denitrification achieved at the cathode in a bioelectrochemical reactor (BER), most of the studies were carried out with an artificial wastewater. Of particularly practical interest to us is the attempt to apply this concept for treating nitrate-laden coking wastewater effluent. The bacteria grown on the cathode play an important role in catalyzing the electrochemical reduction of nitrate; however, they are possibly susceptible to poisoning by the residual biorefractory compounds in the effluent.

In this study, we provided the first example of using an ion-exchange membrane bioelectrochemical reactor (IEMBER), analogous to ion-exchange membrane bioreactor [12–14], for removal of nitrate in the biological effluent from a coking wastewater treatment plant. The IEMBER was composed of three chambers, with a two-chamber BER controlled by a potentiostat and a wastewater chamber, as illustrated in Fig. 1. The proposed concept is an integrated process that combines the transport of nitrate through an anion-exchange membrane (AEM) with its bioelectrochemical reduction in a separate cathode

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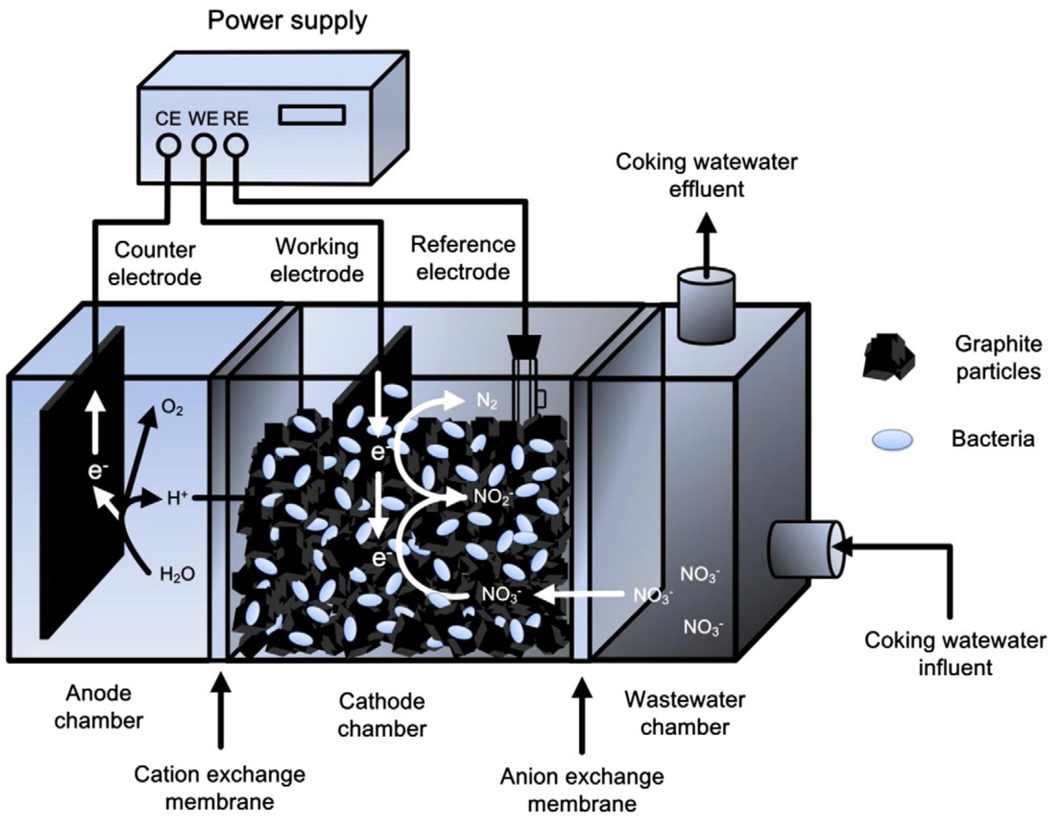

Fig. 1. Schematic diagram of an IEMBER for reduction of nitrate in a coking wastewater.

chamber by the autotrophic denitrifying bacteria. The toxic residuals available in the wastewater chamber were not allowed to pass through the membrane, thus avoiding their potential toxicity to the cathodic denitrifying bacteria.

2. Materials and method

2.1. BER setup

The two-chamber BER made of Perspex frames was fabricated as described previously [11,15], consisting of an anode chamber and a cathode chamber separated by a cation-exchange membrane (CEM, Zhejiang Qianqiu Group Co., Ltd., China). Each chamber contained a bare graphite felt electrode (6.0 cm in diameter and 0.5 cm in thickness) with a Ti wire (0.6 mm in diameter) inserted inside it to allow the external circuit connection. The conductive graphite granules with diameter between 3 and 5 mm (Beijing Sanye Co., Ltd., China) were packed into the cathode chamber, and were connected to the circuit by direct contact with the graphite felt. Here, the 3-D particulate bed electrode was used in order to enlarge the surface area available for the bacterial attachment. The ohmic resistance of the bed cathode was not larger than 2 Ω, as indicated by the high frequency intercept with the x-axis in the EIS (data not shown). After filling with graphite granules, the liquid-phase volume at the cathode reduced to 110 mL.

The three-chamber IEMBER comprised a two-chamber BER and a wastewater chamber which was connected with the cathode chamber by an AEM (Zhejiang Qianqiu Group Co., Ltd., China). The thickness, electrical resistance, permselectivity, total exchange capacity and water permeability are 0.30 ± 0.02 and 0.26 ± 0.02 mm, 3.5 and 2.6 $\Omega\ cm^2$, 98% and 98%, and 0.1 and 5 $mL\ h^{-1}\ cm^{-2}\ MPa^{-1}$, corresponding to the CEM and the AEM respectively. The projected surface area of both membranes used in this study was 28 cm^2.

2.2. Enrichment culture and BER operation

The culture used for the enrichment of denitrifying bacteria in the cathode was the same as that depicted in our previous study [11]. The basal medium contained elements including 0.41 $g\ L^{-1}$ NH_4HCO_3, 0.25 $g\ L^{-1}$ K_2HPO_4, 2.70 $g\ L^{-1}$ $NaHCO_3$, 0.005 $g\ L^{-1}$ $Ca(OH)_2$ and 10 $mL\ L^{-1}$ mineral solution.

The chronoamperometry tests were performed in a three-electrode mode, with the cathode, anode and saturated calomel electrode (SCE) that was inserted into the cathode chamber as the working electrode, counter electrode and reference electrode, respectively. A CHI1030 potentiostat (Shanghai CH Instrument Company, China) was used to control the cathode potential. For the bioelectrochemical batch experiments, the cathode chamber was inoculated with supernate of the enriched culture and the anode chamber was filled with standard basal medium. The cathode potential was set to −0.50 V (vs. SCE), similar to the value reported in other studies concerning the bioelectrochemical reduction of perchlorate [16] or nitrate [7,11]. For the two-chamber BER, two independent bioelectrochemical experiments were conducted with the cathode fed with 20 $mg\ L^{-1}$ nitrate and the biological effluent from a coking wastewater treatment plant (Shaogang, Guangdong Province of China), respectively. The volume ratio of the coking wastewater to the supernate solution present in the cathode chamber was 1:4, and the desired amount of nitrate was amended to make the nitrate concentration contained in the mixture equal to 20 $mg\ L^{-1}$. For the three-chamber IEMBER, the cathode chamber was fed with the supernate and the wastewater chamber was fed with the coking wastewater effluent containing 72 $mg\ L^{-1}$ nitrate. For all the bioelectrochemical tests, the system was equilibrated