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A novel bioelectrochemical method for real-time nitrate monitoring

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ABSTRACT

Nitrate is one of the most common pollutants in the water environment. A key factor for the effective control and removal of nitrate is the ability to accurately determine the nitrate concentration in groundwater and the secondary effluent of wastewater treatment plants. Here, a bioelectrochemical method for real-time detection of the nitrate was developed. In this work, a kinetic model was developed to describe the correlation between the nitrate concentration and the current. Standard addition experiments showed the relative error between indicator predictions and ion chromatographic values ranged from 3.14% to 9.74%. The monitoring results of secondary effluent showed that the system could give a good response at different nitrate concentrations. The average error of not >10.85% between the indicator predictions and ion chromatographic values was demonstrated. This study offers a new method for the development of sustainable bioelectrochemical system (BES)-based technology for the real-time detection of nitrate in groundwater and the secondary effluent.

1. Introduction

Nitrate is ubiquitous in groundwater and the secondary effluent of wastewater treatment plants, in which the biodegradable organic matter is negligible [1–4]. It causes great harm to the natural environment, such as lake eutrophication and red tides in the ocean [5,6], and shows the toxicity when it is transformed into nitrite by microorganisms. Nitrate has received great attention as an important symbol of water pollution among both scholars and the wider public [7], and that is one of the important indexes in water environment monitoring [8,9].

Due to the significant environmental harm of nitrate nitrogen, its determination and monitoring in industrial sewage and drinking water are of utmost importance. However, it is difficult to directly detect nitrate in a simple and inexpensive manner, due to its physical and chemical properties [10]. Various methods for the detection of nitrate have been used, such as ultraviolet spectrophotometry, ion chromatography, cadmium column reduction, and electrochemical analysis [11,12]. The ultraviolet spectrophotometric method is widely used due to its reliability, briefness and low cost [13], but some influence factors restrict its more extensive usage, such as chloride, ammonia and other interfering substances [14]. Ion chromatography has the advantages of simple operation, good sensitivity, and good application prospects in some trace determination [15], but its application is limited due to the high price and high maintenance costs. The disadvantage of the cadmium column reduction method is a high workload and complex operation. Over recent decades, bioelectrochemical systems have attracted great interest due to their unique advantages in the monitoring of water quality. For example, Jin et al. developed a bioelectrochemical volatile fatty acid biosensor on the basis of the microbial desalination cell [16]. Microbial Fuel Cell (MFC)-based biosensors have been applied for the analysis of biochemical oxygen demand (BOD) and biodegradable organic matter and the detection chemical oxygen demand (COD) [17–19]. These electrochemical methods have numerous advantages such as a fast detection speed, wide measurement range and being easy to carry [5,20]. However, because of the high negative potential of nitrate ions on the bare electrode, the electrode is usually modified with noble metal catalysts or a biological enzyme, which limits the application in actual water quality monitoring [21–23]. Therefore, there is a growing demand for the development of a sustainable, simple and cost-effective method for the real-time monitoring of nitrate.

So far, very few attempts have been made to detect nitrate by using bioelectrochemical technology. The aim of the present study is to explore whether a sustainable, simple, low-cost, and real-time indicator based on bioelectrochemical technology can be developed and provide give rapid signals regarding the nitrate in sewage effluent and underground water. In this work, we report a novel approach for the real-time monitoring of nitrate via the competitive relationship between microbial denitrification and electrogenesis processes (Scheme 1). The development of the indicator opens up a new method

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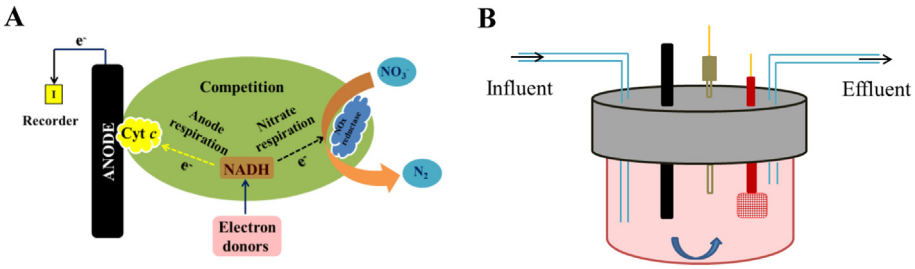

Scheme 1. Schematic illustration of the nitrate real-time indicator.

for the real-time indication of nitrate, extending the application of bio-electrochemical technology.

2. Model description

Marcus et al. proposed the Nernst-Monod model for describing bacterial kinetics, considering that the bio-anode served as the sole electron acceptor, written as follows [24,25]:

$$I = I_{max}\left(\frac{1}{1+\ \exp\left(-\frac{F}{RT}(E_{anode}-E_{KA})\right)}\right)\left(\frac{S_d}{K_d+S_d}\right) \quad (1)$$

where I is the current produced by the electron donor, I_{max} is the maximal current produced by the electron donor, S_d is the concentration of the electron donor ($mg\cdot L^{-1}$), K_d is the half-maximum rate constant for the electron donor ($mg\cdot L^{-1}$), F is the Faraday constant ($96{,}485C\cdot mol^{-1}$ electrons), R is the ideal gas constant ($8.3145\ J\cdot mol^{-1}\cdot K^{-1}$), T is the Kelvin temperature (K), E_{anode} is the potential of the anodic electron acceptor (V), and E_{KA} is the anodic acceptor potential for the half maximum rate (V).

If only electron donors were added, it could be assumed that the current was directly related to the electron donors consumed (Quek et al., 2015). However, the current would be affected if other electron acceptors of higher redox potential such as nitrate are present. Competitive inhibition can be incorporated through a modifier on the K term, which increases the effective K value for the electron acceptor when the competitive electron acceptor concentrations are high relative to the inhibitor's K [26]. The Nernst-Monod model, considering of competitive inhibition, is as follows:

$$I = I_{max}\left(\frac{1}{1+\left(1+\frac{C}{K_c}\right)\ \exp\left(-\frac{F}{RT}(E_{anode}-E_{KA})\right)}\right)\left(\frac{S_d}{K_d+S_d}\right) \quad (2)$$

The concentration inside the reactor is similar to the influent concentration, when the flow rate of the feed solution is large enough. Then, eq. (2) can be written as follows:

$$I = I_{max}\left(\frac{1}{1+\left(1+\frac{C_{in}}{K_c}\right)\ \exp\left(-\frac{F}{RT}(E_{anode}-E_{KA})\right)}\right)\left(\frac{S_{in}}{K_{in}+S_{in}}\right) \quad (3)$$

Eq. (3) is used for describing the response of anode-respiring bacteria to the electron donor in the presence of a competitive electron acceptor such as nitrate. Where K_c is the half saturation inhibitor concentration ($mg\cdot L^{-1}$), S_{in} and C_{in} are the electron donor and competitive electron acceptor concentration, respectively ($mg\cdot L^{-1}$). The values to be determined for this equation include the half-saturation potential E_{KA} of the anode electron acceptor, the maximum current I_{max}, the half-saturation constant K_{in} of the electron donor, and the half-saturation constant K_c of the electron acceptor.

3. Materials and methods

3.1. The construction and operation of the bioelectrochemical indicator

The bioelectrochemical indicator consisted of single transparent perspex chamber, equipped with a multichannel potentiostat (1030C, CH Instruments, Inc., U.S.). The total empty volume for the chamber was 60 cm^3. The graphite rods (approximately 6 cm in diameter and 15 cm in length) were punctured through the rubber stopper and deployed into the chamber as current collectors. An Ag/AgCl electrode (197 mV vs. standard hydrogen electrode, SHE) was employed as the reference electrode to measure anode potential. Platinum mesh (100 mm^2) was employed as the counter electrode. All the parts of the rubber stopper that contacted the graphite rods, reference electrodes, counter electrodes and chambers were well sealed by epoxy glue. Some studies showed that high constant anode potential could achieve higher sensitivity [27,28]. In this work, the bioelectrochemical indicator was connected to a potentiostat to control the working electrodes potential maintained at −0.2 V (vs. Ag/AgCl electrode).

To start-up the indicator, two parallel bioelectrochemical reactors were operated. In the acclimation stage of the electrode biofilm, a 30 mL mixture of potassium nitrate (2.2 ± 0.1 mM) and sodium acetate(1.6 ± 0.1 mM, as sole electron donor) amended nutrient medium (50 mM PBS, 0.13 $g\cdot L^{-1}$ KCl, 1 $mL\cdot L^{-1}$ Wolf's vitamins, 1 $mL\cdot L^{-1}$ Wolf's trace elements, pH = 7) were filled into the chamber, which was then inoculated with 10 mL of active sludge (obtained from a domestic wastewater treatment plant, Beijing, China) and the effluent (20 mL) from a sodium acetate feeding bioelectrochemical indicator. After standing for a certain period of time, the sodium acetate amended nutrient medium as the only electron donor was pumped into the electrochemical reactor at a constant flow rate. The current-time curve was

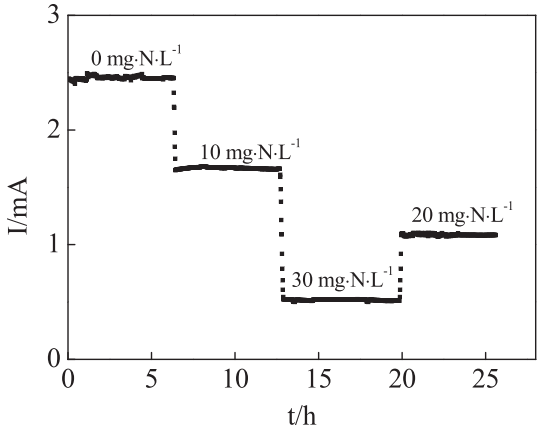

Fig. 1. Effect of the nitrate concentration on the response current.