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The effect of carbon sources on nitrogen removal performance in bioelectrochemical systems

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HIGHLIGHTS

- Coupling the electrogenesis and hydrogen production of electrode to nitrogen removal.
- Contribution rate of autotrophic and heterotrophic denitrification was investigated.
- Influence of organic carbon sources on coulombic efficiency of BES was studied.

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ABSTRACT

In order to ascertain the effects of different carbon sources (methanol, glucose, starch and $NaHCO_3$) on denitrification in BESs, the experiment was conducted in a constant current, 3.5 of chemical oxygen demand to nitrate ratio in a greenhouse. Among the four carbon sources investigated in BESs, $NaHCO_3$ showed the highest nitrite accumulation and the ratio of soluble microbial products to soluble chemical oxygen demand (SMP/SCOD) with a value of 3.68 ± 0.68 mg/L and 94%, respectively. And the addition of organic substrates could reduce SMP production and enhance the denitrification process. In the constant voltage experiment, it was observed that the organics could be used by microbes to generate electrons at the anode. And a maximal current value of 11.0 mA in the BESs fed with starch indicated that the complex carbon source was easier to be used by microorganisms to generate electricity than the simple carbon source.

1. Introduction

Traditional biological processes are widely used in treating wastewater because of their low cost and high treatment efficiency. However, as a result of efforts to improve environmental quality and the emergence of novel contaminants, conventional biological processes can be no longer relied on to meet the required environmental standards. In recent decades, electric current has been used in wastewater treatment to enhance the biological degradation of pollutants. The combination of biology and electrochemistry is thus a novel approach to wastewater treatment and bioelectrochemical systems (BESs) are now being widely investigated by researchers. BESs are unique systems capable of converting the chemical energy of organic waste, including low-strength wastewaters and lignocellulosic biomass, into electricity or hydrogen/chemical products (Pant et al., 2012).

The microbial electrolysis cell (MEC) is one kind of BES; it was developed on the basis of the microbial fuel cell by applying a small voltage (>0.2 V in practice) between the anode and the cathode (Logan et al., 2008). The intrinsic mechanism of the MEC is the generation and transmission of electrons. MECs are efficient for organic degradation and hydrogen production. The focus of research has changed from easily degraded wastewater to refractory wastewater. In the MEC, the key microbial degrading enzyme system may be activated in the presence of an electric current, and some recalcitrant wastes can be effectively removed due to the simultaneous and cooperative roles of biological treatment, electrolytic dissociation and electrochemical oxidation/reduction (Huang et al., 2011). When MECs are applied to protein or cellulose wastewater treatment, the chemical oxygen demand (COD) removal efficiency can reach 85%, and the rate of hydrogen production is about 470–980 mL/g COD (Lalaurette et al., 2009; Lu et al., 2010; Wang et al., 2010). These results indicate that the MEC is promising in terms of contaminant degradation and energy production.

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Another type of BES is the biofilm-electrode reactor (BER). It operates in a similar way to the MEC and has been developed to treat nitrate-contaminated water. BERs reduce nitrate to nitrogen gas by using hydrogen that is produced in situ as the electron donor, nitrate as the electron acceptor, and carbon dioxide as the carbon source. The process has small biomass yield and does not need organic substrates (in contrast to heterotrophic denitrification). In addition, BERs are relatively easy to target to the exclusion of undesirable processes (Smith et al., 2005; Zhang and Lampe, 1996). Research into BERs has mostly concentrated on nitrate removal at the cathode; however, the degradation of organic substrates most likely occurs at the anode, but this aspect of BERs has not been considered in depth.

Conventional BER systems achieve a high utilization rate by microorganisms of the hydrogen produced by electrolysis of water. According to several studies, the current utilization efficiency is higher than 100%, and values have been reported as high as 227% (Zhou et al., 2007). From the point of view of energy transfer, 100% energy utilization is unreasonable. Furthermore, it has been reported that 1 mol of electrons can reduce 0.2 mol of nitrate to nitrogen gas (Shahnaz Islam, 1998). It is clear that, in addition to autotrophic denitrification, some other pathways such as assimilation of cell synthesis and heterotrophic denitrification as a result of cell autolysis probably contribute to the high levels of nitrate removal efficiency.

In BESs, the micro-mechanism of electron transfer between organisms and the electrode is still unclear. Electrons can be transferred to the anode by electron mediators or shuttles (Rabaey et al., 2005), by direct membrane-associated electron transfer (Bond and Lovley, 2003), by so-called nanowires produced by bacteria (Reguera et al., 2005) or perhaps by other as yet undiscovered means. But at the cathode, the way in which electrons are conveyed to the bacteria has not yet been studied (Rabaey et al., 2007).

MECs and BERs are not significantly different in structure. In MECs, the emphasis is placed on organic degradation and hydrogen production by applying a low voltage. But in BERs, the emphasis is placed on nitrate removal through an autotrophic denitrification process. The coupling of MECs and BERs in a reactor is possible because of the similarity of their structures. Organic substrates are degraded at the anode, and this fact is possibly beneficial to the production of hydrogen at the cathode and the autotrophic denitrification process is probably strengthened as a result. In addition, heterotrophic bacteria can utilize organic substrates to remove nitrate. It is considered likely, therefore, that BESs can achieve relatively high nitrate removal efficiency.

Most researchers have considered the treatment of nitrate-contaminated wastewater by pure autotrophic denitrification in BESs. To the best of our knowledge, few researchers have investigated cooperative heterotrophic and autotrophic denitrification. In BESs, if organic substrates were added, the electron-transfer process could be strengthened and thereby promote nitrate removal. Rabaey et al. (2003) discovered that glucose can improve the efficiency of electricity generation in microbial fuel cells. This fact is likely the result of electron transfer by the bacteria to the electrode. In the presence of organic substrates, several pathways of electron current transfer probably exist: (1) organic substrates are decomposed through respiration and the electrons are transferred to nitrate directly; (2) some organisms grow on the surface of the electrode utilizing a mesostate and then transfer electrons to the nitrate; (3) the electrons produced through respiration are primarily delivered to the electrode and then are transferred to the nitrate through conductive materials. Zhao et al. (2011) used an intensified biofilm-electrode reactor (IBER), which uses heterotrophic and autotrophic denitrification to treat nitrate-contaminated water. In their further study, they found that heterotrophic and autotrophic denitrification processes occurred more effectively compared with single heterotrophic denitrification or autotrophic denitrification in the IBER (Zhao et al., 2012). It can be deduced from these studies that some organic substrates may be beneficial to nitrate removal in BER systems. However, the specific factors influencing the effects of organic substrates remain unknown.

The objective of this study was to investigate the effects of different carbon sources (methanol, glucose, starch and $NaHCO_3$) on denitrification in BESs and to evaluate the effectiveness of BESs in the treatment of nitrate-contaminated wastewater. The current utilization efficiency is discussed to shed light on the mechanism of nitrate removal in BESs.

2. Methods

2.1. Experimental apparatus

The experimental configuration is shown in Fig. 1. Rectangular graphite electrodes (length 15 cm, width 8 cm) were used in this study. The electrodes were fixed in a cylindroid reactor with an inter-electrode distance of 4 cm. The effective volume of the reactor was 450 mL. Current was supplied by DC power supply. Control reactors were set up in an identical way but with the electrical circuit open.

2.2. Experimental set up

Synthetic wastewater consisting of nutrients and trace elements was used to simulate nitrate-contaminated water in this study. The nitrogen was provided by $NaNO_3$; the NO_3^-–N concentration was maintained at 30 mg L^{-1}. Methanol, glucose and starch were used as organic carbon sources and $NaHCO_3$ was used as an inorganic carbon source. Seed sludge was collected from Qige wastewater treatment plant (Hangzhou, China). The COD to NO_3^-–N ratio and the current were maintained at 3.5 and 5 mA, respectively. The synthetic wastewater was replaced every 24 h and the temperature was maintained at 30 ± 2 °C in a greenhouse. When the total nitrogen (TN) removal efficiency was higher than 60% for more than 5 days, the BES was considered to be stable and experiments were conducted. The nitrogen removal performance was investigated and the effluent components were measured. After the constant-current experiments were completed, a constant voltage of 4.0 V was applied to the BESs with added glucose and with added starch, and the changes in current were investigated.

2.3. Analytical method

All samples were filtrated using a 0.45 μm filter membrane before analysis. NH_4^+–N, NO_3^-–N, TN and NO_2^-–N were measured according to standard methods (APHA, 1998). COD was measured using a DR2800 spectrophotometer (HACH Company, Loveland, CO, USA). pH was measured using a pH meter (Mettler Toledo, Greifensee, Switzerland). The current was measured by an intelligent digital multimeter (UNI-T Company, Shanghai, China).

Glucose was measured according to the standard method (Miller, 1959). Volatile fatty acid was measured by withdrawing a 4-μL sample from the headspace using a gas-tight syringe followed by gas chromatography with a chromatograph (GC 7890, Shanghai Tianmei Science Instrument Co., Ltd., Shanghai, China) equipped with a flame ionization director. The carrier gas was nitrogen, and the detector, injection port and column temperatures were 250, 230 and 180 °C, respectively. The measurement of soluble microbial products (SMPs) is difficult. Following the advice of Barker and Stuckey (1999), SMP was defined as: SMP = SCOD –