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Review

Nutrients removal and recovery in bioelectrochemical systems: A review

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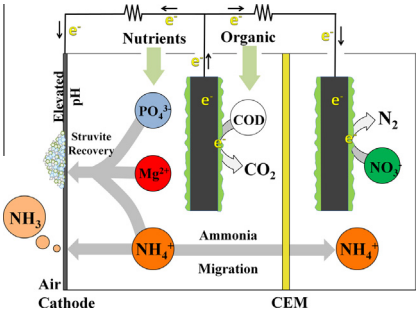
HIGHLIGHTS

- Nutrients are key contaminants to be removed in bioelectrochemical systems (BES).
- Nitrogen is removed by biological and bioelectrochemical reactions.
- Nitrogen is recovered through ammonia migration and volatilization.
- Phosphorus is removed and recovered in precipitates due to high electrolyte pH.
- Effective and efficient nutrients removal/recovery will make BES more competitive.

GRAPHICAL ABSTRACT



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ABSTRACT

Nutrient removal and recovery has received less attention during the development of bioelectrochemical systems (BES) for energy efficient wastewater treatment, but it is a critical issue for sustainable wastewater treatment. Both nitrogen and phosphorus can be removed and/or recovered in a BES through involving biological processes such as nitrification and bioelectrochemical denitrification, the NH_4^+/NH_3 couple affected by the electrolyte pH, or precipitating phosphorus compounds in the high-pH zone adjacent a cathode electrode. This paper has reviewed the nutrients removal and recovery in various BES including microbial fuel cells and microbial electrolysis cells, discussed the influence factors and potential problems, and identified the key challenges for nitrogen and phosphorus removal/recovery in a BES. It expects to give an informative overview of the current development, and to encourage more thinking and investigation towards further development of efficient processes for nutrient removal and recovery in a BES.

1. Introduction

In a bioelectrochemical system (BES), organic compounds are oxidized by microorganisms, and the electrons generated from this oxidizing process can be used to produce energy and other value-added compounds (Wang and Ren, 2013). Direct conversion of chemical energy into electric energy in a BES holds potential advantages over the existing technologies in terms of energy recovery from organic compounds, and the intensive studies of BES configuration/operation, microbiology, electrochemistry, and application have occurred in the past decade. The representative BES includes microbial fuel cells (MFCs), microbial electrolysis cells (MECs), and microbial desalination cells (MDCs). A BES can be potentially applied to treat wastewater, to power remote sensors, to act as a platform for studying fundamental microbial interaction with a solid electron acceptor/donor (e.g., in a micro-MFC), or to produce value-added compounds through electrochemical or electrosynthetic processes.

The use of the low-grade substrates such as wastewater as an electron source is attractive because of the increasing demand for sustainable water/wastewater treatment with a low carbon footprint. Various substrates including pure organics and domestic/industrial wastewaters have been examined in the BES for

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electricity generation (Pant et al., 2010), the BES size has been enlarged from milli-liter to liter-scale or even larger at a pilot scale, and its long-term performance outside the laboratory has been reported (Zhang et al., 2013a). However, at this stage the energy recovery in a BES is still too low to make it practically competitive, and a benchmark power density of 1000 W m^{-3} (Arends and Verstraete, 2012) was realized only in very small-scale reactors. The low energy recovery, as well as the low energy consumption (due to the reduced use of aeration) in a BES, indicates that its primary function, if designed for energy recovery from wastewater treatment, may be contaminant removal, rather than energy recovery that would be a beneficial plus to offset energy use by the treatment process, thereby furthering energy benefits by using BES (He, 2013). In addition, because of a low conversion efficiency (from organic to electric energy), a BES will be more applicable to the low-strength wastewater, such as domestic wastewater.

The main goal of contaminant removal in a domestic wastewater treatment process is to reduce the concentrations of organic pollutants and nutrients (mainly nitrogen and phosphorus). BES can efficiently remove organic compounds within a reasonable time; however, the anaerobic condition in the anode of a BES does not effectively facilitate nutrient removal, which may require aerobic conditions (e.g., nitrification, and enhanced biological phosphorus removal). Therefore, nutrient removal has become a key challenge to develop BES for efficient wastewater treatment. Nitrogen and phosphorus are the key contaminants and also the important elements for improving agricultural production; due to the stricter discharge regulation and the depleting reserve, there is an increasing trend of research and development of wastewater treatment technologies to remove and/or recover nutrients from wastes (Rittmann et al., 2011). A BES capable of removing or recovering nutrients will certainly make it promising for future deployment. The objectives of this review paper are to examine the past research on nutrient removal/recovery in BES (with a focus on wastewater treatment), introduce developed technologies, analyze removal efficiencies, and discuss the challenges for future development of BES for effective and efficient nutrient removal and/or recovery. The studies of nitrogen removal in biofilm-electrode reactors (BERs) are excluded because the denitrification in a BER relies on *in situ* produced hydrogen gas as an electron donor (Ghafari et al., 2008), which is different from a BES described here.

2. Nitrogen removal and recovery

2.1. Effect of nitrogen on BES performance

Nitrogen can affect the BES performance, especially electricity generation, through inhibiting effects on microbes, adjusting pH, and competition for electron donors/acceptors. It was reported that a concentration of total ammonia nitrogen (TAN) higher than 500 mg L^{-1} could severely inhibit power production, and the maximum power density decreased from 4.2 to 1.7 W m^{-3} when the TAN concentration increased from 500 to 4000 mg L^{-1} (Nam et al., 2010). It was concluded that a high concentration of free ammonia nitrogen had inhibited the activity of the anode-respiring bacteria. The researchers further demonstrated ammonia inhibition in a continuously-operated MFC, in which the maximum power density dropped from 6.1 to 1.4 W m^{-3} when the TAN concentration increased from 3500 to 10,000 mg L^{-1} (Kim et al., 2011). By comparing with their previous study of the batch MFCs, the researchers found that the microorganisms in a continuously-operated MFC could adapt to a much higher TAN concentration. Ammonia inhibition is affected by the anolyte pH, and a low anolyte pH results in less free ammonia and thus little inhibitive effect; this was demonstrated in a two-chamber MFC, in which increasing the concentration of ammonium nitrogen from 70 to 4000 mg L^{-1} at a neutral anolyte pH did not affect the MFC performance (Kuntke et al., 2011).

It is clear that the electrolyte pH in a BES is a key parameter, because of its effects on microbial metabolism and overpotential. Nitrogen compounds can influence the electrolyte pH through biological and chemical reactions. Biological nitrification releases protons that could buffer the high pH of a catholyte due to oxygen reduction, as demonstrated in an MFC with a buffer-free catholyte: adding the nitrifying bacteria and ammonium into the catholyte improved the voltage from 0.30 to 0.56 V and decreased the catholyte pH from 8.8 to 7.0 (You et al., 2009). Further studies by others confirmed that nitrification activity in the cathode could consume alkalinity and lower the pH (Virdis et al., 2010; Zhang and He, 2012b). The NH_4^+/NH_3 couple was used to control the electrolyte pH: the ammonium ions were added into the anode compartment and then migrated into the cathode compartment across a cation exchange membrane to buffer the high pH; the volatilized NH_3 was returned to the anode compartment to maintain a reasonable anolyte pH. In this way, the NH_4^+/NH_3 couple acts as a proton shuttle between the anode and the cathode compartments (Cord-Ruwisch et al., 2011). This concept was further developed by employing an MEC and an additional gas exchange device to use hydrogen gas for driving the ammonia recycle (Cheng et al., 2013). Such a change promoted ammonia migration by current generation and developed a more efficient anodic biofilm.

Nitrogen compounds could also negatively affect the BES performance via competing for electron donors (e.g., organics) or acceptors (e.g., oxygen) with microorganisms or electrodes. It was reported that in a single-chamber MFC, the presence of 4–8 mM nitrate decreased electricity generation, especially at lower external resistance where high current generation (and thus more electrons flowing) was expected (Sukkasem et al., 2008), likely due to the competition for electrons (in organic compounds) between the anode electrode (anode-respiring bacteria) and nitrate (denitrifying bacteria). Nitrification of ammonium in a cathode compartment may cause competition for oxygen between nitrifying bacteria and the cathode electrode, as shown in a two-chamber MFC, in which increasing ammonium concentration from 30 to 100 mg L^{-1} (while maintaining a constant organic loading rate) decreased the cathode potential (Ryu et al., 2013).

Therefore, understanding of the nitrogen effects on BES performance is critical to maintain a healthy operation, and proper control of the nitrogen effects will be necessary under certain conditions. Development of effective nitrogen removal and recovery strategies will not only reduce the negative influence of nitrogen on BES performance, but also eliminate the contaminants and/or recover valuable nutrient resources.

2.2. Nitrogen removal

2.2.1. Background

Nitrogen is removed from wastewater usually by using biological processes such as nitrification (ammonia oxidized to nitrate) and denitrification (nitrate reduced to nitrogen gas) (Knowles, 1982). Ammonia can also be anaerobically oxidized, for instance using nitrite as an electron acceptor in an ANAMMOX process (Jetten et al., 2001), and this process can theoretically generate a positive electric potential under a standard condition; however, this thermodynamically favored process has a very slow kinetics to be realized in a BES (He et al., 2009). Although a recent study reports an ANAMMOX-like process in an MEC (Zhan et al., 2012), further evidence will be required to prove the feasibility of anaerobic ammonia oxidation with an electrode as an electron acceptor in the presence of low dissolved oxygen. Therefore, ammonia removal in a BES is mainly through ammonia loss across a separator (Kim et al., 2008), or nitrification with supply of oxygen.