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Recent Advances in Nitrogen Removal from Wastewater Using Bioelectrochemical Systems

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Abstract: *Bioelectrochemical systems (BESs) have recently gained great attention as a promising technology that generates electricity, hydrogen, or other useful chemicals by oxidizing biodegradable organic matters using electrochemically-active bacteria. During the last few decades, numerous studies have been successfully carried out in the field of BESs for increasing its wastewater treatment performance. However, most studies focus on only removing organic matter from wastewater using BESs. Nevertheless, the main objective of wastewater treatment is to remove organic matter besides nutrients since nitrogen is one of the key contaminants found in wastewater. Discharging of untreated or inadequately treated wastewater may introduce an excessive amount of nitrogen species into natural waters, which can cause excessive growth of algae. Excessive algae growth promotes eutrophication of rivers, lakes, and coastal waters, which impairs the quality of water resources. Even though there is limited research investigating nitrogen removal in BESs, several studies demonstrated that nitrogen can be transformed and/or removed using BESs. After considering the significance of nitrogen removal and increasing environmental concerns related on it, which summarized above, this study summarizes the recent development of nitrogen removal using BESs. Moreover, general design and operational principles of the BESs, application areas, advantages, and challenges were summarized beside different BES reactor configurations.*

Keywords: *bioelectrochemical systems, nitrogen, wastewater treatment*

Introduction

Bioelectrochemical systems (BESs) have recently gained great attention as a promising technology that generates electricity, hydrogen, or other useful chemicals by oxidizing biodegradable organic matters using electrochemically-active bacteria (Pant, Singh et al. 2012). BESs have been studied for a variety of applications, including microbial fuel cells (MFCs) for electricity generation, microbial electrolysis cells (MECs) for hydrogen generation, microbial desalination cells (MDCs) for water desalination, microbial electrosynthesis systems (MESs) for chemical production, and microbial methanogenesis cells (MMCs) for methane production (Aelterman, Rabaey et al. 2006, Cao, Huang et al. 2009, Parameswaran, Torres et al. 2011, Marshall, Ross et al. 2012). Even though BESs have diverse applications, they have the same principle with a simple electrochemical cell.

Among all BESs, the microbial fuel cell (MFC) is the most studied type and the main goals of MFCs are electricity generation and wastewater treatment (Liu, Ramnarayanan et al. 2004, Aelterman, Rabaey et al. 2006, Santoro, Arbizzani et al. 2017). Even though many different configurations are possible for MFCs, but a typical MFC consists of two chambers (Figure 1). In the anodic chamber of an MFC, electrochemically active bacteria oxidize organic matter to generate electrons and protons. The generated electrons are transferred to electrodes. In the meantime, the protons diffuse from the anode to the cathode through a separator. At the cathode chamber of an MFC, the electrons combine with the protons to reduce the electron acceptor (usually oxygen) (Logan, Hamelers et al. 2006). A schematic diagram of an MFC is shown in Figure 1.

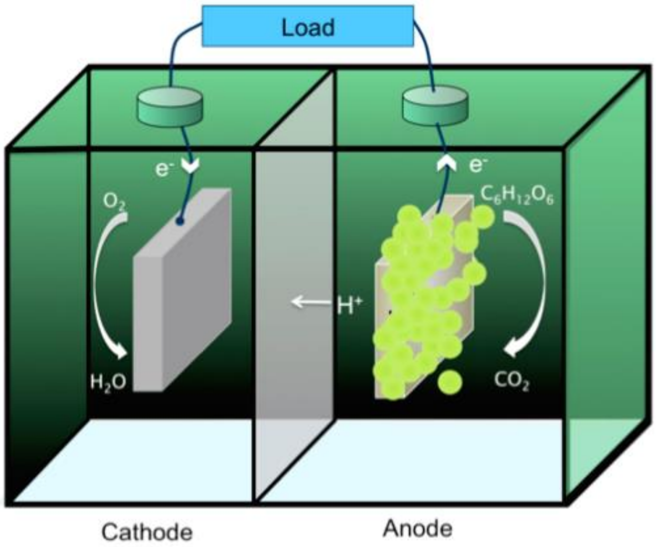

Figure 1. Schematic representation of a microbial fuel cell

For example, if glucose ($C_6H_{12}O_6$) is used as an electron donor (298 °K, 1 bar, pH=7) and oxygen is the electron acceptor, the reactions occurring in each electrode can be expressed as in Eqs. (1) - (2) below:

Oxidation reaction at anode:

$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^-$ $\quad E^o = -95\ mV_{Ag/AgCl}$ (1)

Reduction reaction at cathode:

$6O_2 + 24H^+ + 24e^- \rightarrow 12H_2O$ $\quad E^o = 1030\ mV_{Ag/AgCl}$ (2)

The theoretical total cell potential (E^o_{cell}) is calculated as the potential difference between the cathode potential (E^o_{cat}) and anode potential (E^o_{an}) using the formula: $E^o_{cell} = E^o_{cat} - E^o_{an}$. Hence, the theoretical cell potential is 1125 mV vs. Ag/AgCl when glucose is used as a model electron donor (Logan 2008).

Another of the most investigated BESs is the MEC. The basic difference between an MFC and an MEC is the reduction reactions at the cathode. In the MEC, protons are reduced with a supply of additional voltage since the reaction is not spontaneous, and it needs additional voltage to complete the reaction, and for hydrogen gas. In addition, the MDC has been developed as an extension of MFC technology for simultaneous wastewater treatment, water desalination, and electricity generation. A typical three-chambered MDC consists of a cathode chamber, a desalination chamber, and an anode chamber (Gude, Kokabian et al. 2013). The desalination chamber is placed in the middle of the MDC and connected to a cation exchange membrane (CEM) and an anion exchange membrane (AEM). If an individual electrode is chosen for a study, the BES consists of only one working electrode with a reference and a counter electrode; this system is called a three-electrode system. In a three-electrode system, the working electrode is anode, where the reaction of interest occurs, the reference electrode (RE) provides a stable reference potential to measure the potential of the working electrode (WE), and the counter electrode (CE) is cathode, which used to complete the overall reaction in an electrochemical cell (Beyenal and Babauta 2015).

Significant advances have been made in wastewater treatment using BESs during last years. However, most studies focus on only removing organic matter from wastewater using BESs.

Nevertheless, the main objective of wastewater treatment is to remove organic matter besides nutrients. Nitrogen is one of the key contaminants found in wastewater, where it exists in the reduced forms of ammonia (NH_3 or NH_4^+) and organic nitrogen (Rittmann and McCarty 2012). Discharging of untreated or inadequately treated wastewater may introduce an excessive amount of nitrogen species into natural waters, which can cause excessive growth of algae. Excessive algae growth promotes eutrophication of rivers, lakes, and coastal waters, which impairs the quality of water resources (Anup, Woo-Chang et al. 2011). The current conventional nitrogen removal processes are based on activated sludge processes. The activated processes are costly because of the need for extensive aeration during nitrification, in which ammonium (NH_4^+) is oxidized to (NO_3^-) nitrate. Also, in anoxic denitrification, in which NO_3^- is reduced to dinitrogen (N_2), sometimes requires external organic carbon additions. Furthermore, these processes can produce nitrous oxide emissions during nitrogen removal contributes to global warming (Tchobanoglous, Burton et al. 2003, Kuypers, Marchant et al. 2018). That's why it is important to investigate other methods to reduce the negative effects of the current treatments.

During the last few decades, numerous studies have been successfully carried out in the field of BESs for increasing its wastewater treatment performance. Even though there is limited research investigating nitrogen removal in BESs, several studies demonstrated that nitrogen can be transformed and/or removed using BESs. After considering the significance of nitrogen removal and increasing environmental concerns related on it, which summarized above, this study summarizes the recent development of nitrogen removal using BESs. Moreover, general design and operational principles of the BESs, application areas, advantages, and challenges were summarized beside different reactor configurations.

Nitrogen Removal Processes in Bioelectrochemical Systems

Most nitrogen in wastewater is in the form of NH_4^+, so the current conventional systems are mostly designed nitrification process prior to denitrification process for nitrogen removal. As mentioned above, most of the BESs studies, which investigated nitrogen removal, were adapted this process in MFCs with air cathode using different reactor configurations and operational parameters. Several studies demonstrated that nitrogen can be transformed and/or removed using BESs (Mousavi, Ibrahim et al. 2012, Park, Park et al. 2017). Most of these studies were based on MFCs with an air-cathode configuration, in which nitrification takes place on the surface of the air cathode to oxidize ammonia and ammonium (Equation 3) and that heterotrophic and/or autotrophic denitrification may contribute to complete nitrogen removal in anodic compartment (Equation 4) (Figure 1).

$$NH_4^+ + NO_2^- \rightarrow N_2 + H_2O \quad (3)$$

$$2NO_3^- + 10e^- + 12H^+ \rightarrow N_2 + 6H_2O \quad (4)$$

Common configurations include single chamber MFCs (Yan, Saito et al. 2012), dual chamber MFCs (Virdis, Rabaey et al. 2010), stackable horizontal MFCs, flat-panel air cathode MFCs (Park, Park et al. 2017), and flat MFCs with a membrane bioreactor (Zhang, Zhu et al. 2013). The first demonstration was conducted by Virdis et al. using a separate biofilm aerobic reactor to oxidize NH_4^+ to NO_3^- (Virdis, Rabaey et al. 2008). In this study, wastewater first enters the anode compartment of the MFC in which acetate oxidation takes place. Then, the effluent from the MFC enters the biofim aerobic reactor in which nitrification occur there. In final stage, the wastewater return to the MFC for denitrification in which NO_3^- was reduced to N_2 in the cathode. Even though they successfully achieved simultaneous carbon and nitrogen removal, elevated ammonium concentration in the final effluent due to diffusion from anode compartment to cathode compartment through the cation exchange membrane was the limitation of this study. Their following study aimed to integrate the nitrification process in the cathode compartment of the MFC in which simultaneous nitrification and denitrification (SND) was accomplished (Fig.1.A) (Virdis, Rabaey et al. 2010). Zhang et al. used a single chamber MFC with a rotating biocathode to remove nitrogen and carbon simultaneously (Fig.1.B) (Zhang, Zhang et al. 2013). The novel part of this study was that nitrification was supported by the outer biofilm of the biocathode while denitrification was occurred inner anoxic environment. Therefore, this study confirmed that it is possible to achieve over 90% of TN removal using with a rotating biocathode in a single chamber MFC. Yan et al. also studied combined nitrification-denitrification mechanisms in a different MFC reactor configuration (Fig.1.C) (Yan, Saito et al. 2012). The novel part of this study the air cathode of a single chamber MFC was pre-enriched with a nitrifying biofilm on the surface of the air cathode and also diethylamine-functionalized polymer was used as a Pt catalyst. The authors conclude that diethylamine-functionalized polymer binder accelerated nitrifier biofilm enrichment, so 93.6% of nitrogen removal efficiency was achieved using it. Park et al. used completely different MFC configuration, which is a flat panel air cathode MFC contained five MFC units in series, to remove organic and nitrogen from wastewater (Fig.1.D) (Park, Park et al. 2017). Also, this study performed a long period of time, which was a proof of that concept can be a promise nitrogen removal technology. The common property of these studies is that nitrification takes place on the surface of the air cathode to oxidize ammonia NH_3/ NH_4^+ and that heterotrophic and/or autotrophic denitrification may contribute to the complete nitrogen removal (Fig. 2). However, most of these studies did not reported outlet NH3-N, NO_2^--N and NO_3^--N concentrations although all nitrogen species should take into account because of their detrimental effects on environment and human health.

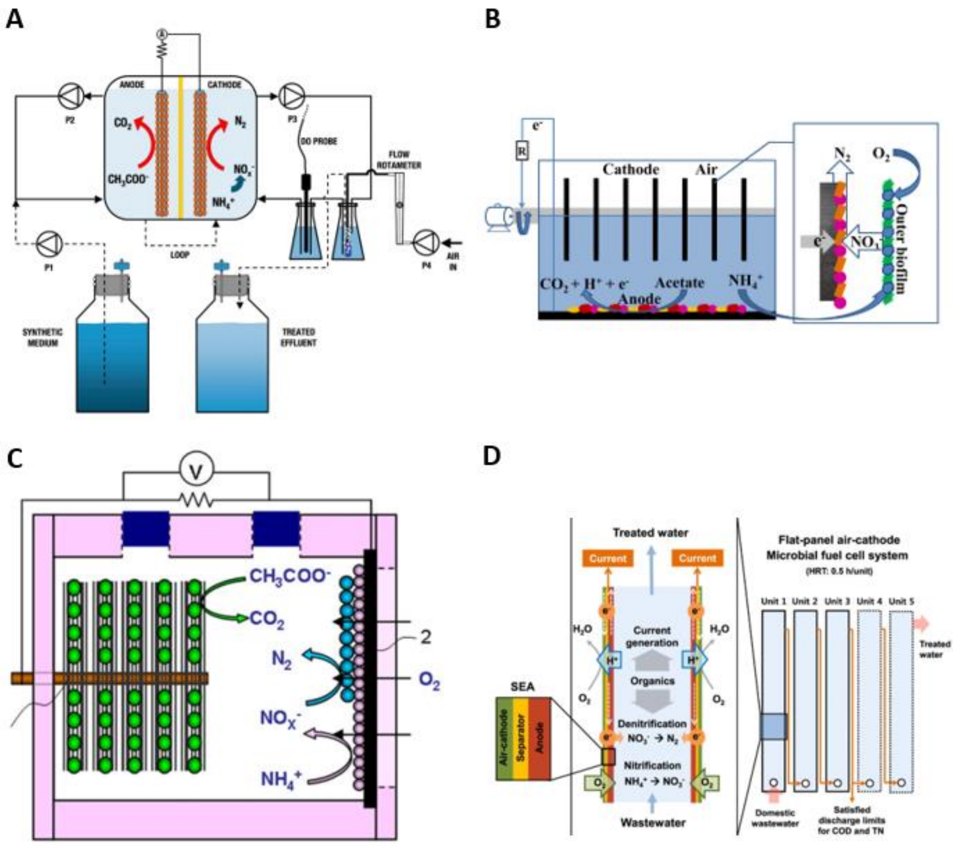

Figure 2. The MFCs designed for nitrogen removal involving nitrification and denitrification processes (Virdis, Rabaey et al. 2010, Yan, Saito et al. 2012, Zhang, Zhang et al. 2013, Park, Park et al. 2017)

As mentioned in the previous section, three-electrode system is generally used if we would like to investigate the electron transfer mechanism between the microorganism and the individual electrode to obtain a fundamental level of knowledge. That's why if anodic and cathodic biofilms were investigated separately, the nitrogen mechanisms can be explained more understandable. Besides nitrogen and denitrification mechanisms, nitrogen can be removed in other mechanisms. One of the other possible mechanisms of nitrogen removal is ammonia volatilization (Equation 5), which is the conversion of NH_4^+ ions into ammonia gas in highly elevated pH (Kim, Zuo et al. 2008).

$$NH_4^+ \rightarrow NH_3 + H^+ \quad (5)$$

NH_4^+ ions have a pKa=9.25, so an increase in pH would result in a re-distribution of ammonium ions to the more volatile NH_3 form. However, pH increase could be always related with ammonia volatilization, different mechanisms also can involve increasing pH such as N_2 bubbling and denitrification (Ketep, Bergel et al. 2013, Hai, Yamamoto et al. 2018).

Assimilated by microorganisms is another mechanism ammonium (Equation 6) (Kuypers, Marchant et al. 2018). The growth rate of aerobic microorganisms in conventional biological treatment systems is relatively higher than the growth rate of anaerobic microorganism (Speece 1983). Therefore, it is expected that the nitrogen removal related to assimilation would be considerable low in bioelectrochemical reactors treating domestic wastewater.

$$4CO_2 + HCO_3^- + NH_4^+ + H_2O \rightarrow C_5H_7O_2N + 5O_2 \quad (6)$$

Also, it has been demonstrated that some of *Geobacter* species were able to reduce nitrate to nitrite with an electrode as the only electron donor (Gregory, Bond et al. 2004). This can also explain that one of the main mechanisms was the nitrate reduction in the BESs reactor. Ammonia can also be anaerobically oxidized in an ANAMMOX process, in which NH_4^+ and NO_2^- react to form N_2 by anammox bacteria (Ma, Wang et al. 2016). There are also some new combine technologies such as shortcut nitrification-denitrification (SND) processes, the single reactor high activity ammonium removal over nitrite (SHARON) process, oxygen-limited autotrophic nitrification–denitrification (OLAND), and completely autotrophic nitrogen removal over nitrite (CANON) processes, which can be successfully applied in BESs (Table 1).

Table 1. Comparison of Various Biological Nitrogen Removal Technologies and Processes

Process	Electron Donor	Electron Acceptor	Temperature (°C)	Operating Conditions
Nitrification	Ammonia or nitrite	Oxygen	5-45	Aerobic (2-3 mg/L)
Denitrification	COD	Nitrate	5-45	Anoxic
Ammonia stripping	-	-	25	Aerobic or Anaerobic
Nitrogen assimilation	-	-		Aerobic or Anaerobic
Bioelectrochemical denitrification	Hydrogen gas Electrode	Nitrate		Anoxic
Anammox	Ammonium	Nitrite	2-43	Anaerobic
Deamox	Sulphide(S^{-2})	Nitrite	12.7 -29.2	Aerobic, then anaerobic
CANON	Ammonia Nitrite	Oxygen -	30-40	Oxygen limited
OLAND	- Ammonium	Oxygen -	30	Oxygen limited

Many factors can affect the nitrogen removal performance in BESs including dissolved oxygen, C/N ratio, pH, and retention time. Among them, one of the critical parameter is dissolved oxygen which should be carefully control. Low DO level can cause NH_4^+ accumulation because of incomplete nitrification while high DO level can inhibit denitrification process. Another important parameter is C/N ratio since organic carbon required for heterotrophic denitrifiers, which increase to removal of nitrate. However, low C/N ratio facilities the conversion of chemical energy into electrical energy. As mentioned before, pH can affect the anodic and cathodic mechanisms, so optimal pH should be adjust to obtain effective nitrogen removal (Sun, Cao et al. 2020).

Conclusion

Because of the current problems of conventional wastewater treatment systems, which are mainly high energy requirement and sludge disposal, the promising concept of BESs for wastewater treatment has recently emerged as an alternative wastewater treatment system. Nitrogen is one of the key contaminants found in wastewater, and also aimed to be removed in BES technology. Therefore, this current study provides an updated summary of the recent development of nitrogen removal using BESs. In addition, general design and operational principles of the BESs, application areas, advantages, and challenges were summarized beside different BES reactor configurations. This study aimed to provide fundamental knowledge and outlines instructions for future studies, and demonstrate that BESs can be a viable wastewater treatment technology.

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