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# Current as an indicator of ammonia concentration during wastewater treatment in an integrated microbial electrolysis cell - Nitrification system

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ABSTRACT

A key challenge for ammonia monitoring during nitrogen removal process is the extra cost and toxic reagent consuming. Herein the feasibility of current generated by an integrated microbial electrolysis cell (MEC) - nitrification reactor as an indicator of initial ammonia levels ($NH_3/NH_4^+$) in wastewater was explored. In this loop system, ammonia was first oxidized to nitrate in the nitrification reactor, and then the effluent was introduced into the cathode of MEC where nitrate was reduced as electron acceptor. The correlation between current and ammonia concentration was first investigated with synthetic ammonia-rich wastewater. A good linear relationship ($R^2 = 0.9419$) was observed between current (0.5130 −3.906 mA) and ammonia levels (0–62.1 mg $NH_4^+$-N/L). Such linear relationship was always obtained regardless of the tested external power supply or wastewater pH. The external electrochemical cell was proved to be an effective pre-conditioning method to remove the disturbance from other possible electron acceptors. Finally, the integrated system was further tested with real waste streams and the results showed no significant difference ($p > 0.05$) with measurements by conventional methods. This study, for the first time, demonstrated the potential application of the integrated MEC - nitrification system for ammonia monitoring in addition to water treatment.



## 1. Introduction

Ammonia, as a notorious toxic environmental pollutant, is produced in various industrial processes such as food industry, fertilizer production, oil refining, steel making and anaerobic digestion, etc [1–3]. High concentrations of ammonia discharged into aquatic water would lead to several environmental issues such as eutrophication of lakes and other water recipients, toxicity to humans, or affecting system performances. Thus, many efforts have been made for ammonia removal and monitoring in the past decades [4–6].

Bioelectrochemical systems such as microbial fuel cell (MFC) have attracted increasing attention in the past decades due to its unique merits in water treatment, energy production, chemical synthesis and environmental monitoring [7–9]. In general, the organics in the anode of MFC are oxidized into electrons, protons and carbon dioxide. The electrons and protons are transferred to cathode to reduce the final electron acceptors, typically oxygen. With this principle, electricity is produced while organic matters are removed from wastewater. Recently, simultaneous carbon and nitrogen removal using an integrated MFC-nitrification loop system has been successfully demonstrated [10]. In such process, the wastewater firstly entered in the anode chamber for organics removal, and then the effluent was directed to an external nitrification reactor where ammonia was oxidized to nitrate. The wastewater was finally returned to the cathode chamber of MFC, where nitrate reduction occurred. In that nitrogen loop system, the removal rates up to 2 kg COD $m^{-3}$ net cathodic compartment (NCC) volume $d^{-1}$ and 0.41 kg $NO_3^-$-N $m^{-3}$ NCC $d^{-1}$ were continuously achieved in the anode and cathode chamber, respectively. Subsequently, nitrification was further integrated into the cathode of MFC by different research groups for simultaneous nitrification, denitrification and carbon removal. With such system, carbon removal efficiency reached 100%, while nitrogen removal efficiency achieved 94%. In MFC, the nitrate was mainly removed via electrochemical reduction in cathodic compartment, which may link the circuit current to nitrate concentrations. Moreover, it was noticed that in previous studies the current generation showed different

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response to different ammonia levels in wastewater influent [11]. Therefore, we hypothesize that the bioelectrochemical system not only has the ability of simultaneous carbon and nitrogen removal, but also could read the ammonia levels from the current generation. If the current could be an indicator of ammonia levels in influent, it would save time and extra cost for an additional ammonia monitoring equipment. The current commercialized ammonia sensor is based on the use of ion-selective electrode, which is strongly affected by the sodium and potassium disturbance [13]. Considering the great advantage of convenience, simplicity, it's come up of the idea of investigation the feasibility of current as an indicator for ammonia levels in MFC loop system.

Based on the above hypothesis, an integrated MEC - nitrification system was developed to explore the feasibility of current as an indicator of ammonia concentrations at the same time of treating the wastewater. In such integrated system, ammonia in the wastewater was firstly oxidized to nitrate through a nitrification reactor. Subsequently, the nitrification effluent was directed to the cathode of MEC for nitrate reduction. Compared to the MFC, the external power in MEC could facilitate the electron transfer between anode and cathode for nitrate reduction, and thus, could greatly reduce the reaction (response) time. Since the main objective was to explore the current response to ammonia levels, the treatment performance was not the focus of this study. To the best of our knowledge, this is the first study to explore the feasibility of using current as an indicator of ammonia concentrations during the nitrogen removal process in such loop system. The current response to different ammonia levels was first evaluated using the synthetic wastewater in terms of nitrification efficiency, ammonia detection range, response time and reproducibility. The effect of different operation parameters (e.g., pH and external power supply) on current response to ammonia levels was explored as well. Moreover, an electrochemical cell [14] was tested as a preconditioning method to exclude the disturbance from other electron acceptors such as nitrate in the waste stream. The results would greatly promote the wide application of such integrated system and simultaneously expand the application niches of microbial electrochemistry.

## 2. Experimental section

### 2.1. Reactor setup and operation

The MEC made of nonconductive polycarbonate plates was a rectangular reactor composed of two chambers (Fig. 1). The anode (100 ml) and cathode (50 ml) chamber were separated by a cation exchange membrane (CEM, CMI 7000, Membrane international, NJ). The whole reactor was assembled with rubber gaskets and sealed with screws to avoid leakages. The electrodes for anode and cathode were carbon brush (5.0 cm in diameter, 5.0 cm in length, Mill-Rose, USA) and a titanium woven wire mesh (4 × 5 cm, 0.15 mm aperture, William Gregor Limited, London) coated with 0.5 mg/cm$^2$ Pt, respectively. The membrane was soaked in 50 mM NaCl solution for 24 h, and then soaked in distilled water prior to use.

To enrich exoelectrogenic biofilm on the anode, the reactor was first operated at MFC mode for about two months. During the enrichment, the anode was inoculated with the wastewater collected from a primary clarifier (Lundtofte Wastewater Treatment Plant, Lyngby, Denmark) with the following characteristics: 1000 mg-COD/L $CH_3COONa$, pH 7.2 ± 0.1, conductivity 2120 ± 4 us/cm, 1.5 ± 0.2 mg $NO_3^-$-N/L, 20.3 ± 0.1 mg $NH_4^+$-N/L. 20 mM sodium acetate was added to provide sufficient carbon source for microorganisms in the anode. 50 mM PBS (pH - 7) solution was used as the catholyte during the enrichment period. The anode and cathode were connected with an external resistance (R = 1000 Ω). After the enrichment period, the reactor was switched to MEC mode. A power supply (NEWARE Battery testing system 7.5.X, China) was used to provide external voltage to the reactor.

A lab-scale nitrification reactor was employed to oxidize the ammonia to nitrate. The nitrification reactor was a glass bottle with volume of 500 ml. The inoculum was collected from the biomass of a membrane bio-reactor (MBR). The total solid of biomass was 2.5 g/L and pH was 7.04. After transferring the biomass into reactor, medium with nutrients necessary for growth of the nitrification bacteria was added. The medium contained 2.45 g/L $NaH_2PO_4$, 4.58 g/L $Na_2HPO_4$, 0.1 g/L KCl, 0.1 g/L $MgCl_2 \cdot 6H_2O$, 0.1 g/L $CaCl_2 \cdot 2H_2O$, 12.5 ml/L mineral solution and vitamin solution as describe before [15]. $NaHCO_3$ (2 g/L) was used as the carbon source and electron donor. The reactor was open to the air and mixing by magnetic stirrer was ensuring aeration of the reactor.

An electrochemical reactor [14] was developed to study the effect of sample pre-conditioning on the sensor performance. The EC reactor was made of nonconductive polycarbonate plates. It was a rectangular reactor composed of anode chamber (50 ml) and cathode chamber (100 ml). The anode was a titanium mesh electrode coated with Ir MMO (dimensions: 4 × 5 cm; 1 mm thickness; specific surface area 1.0 m$^2$/m$^2$, Magneto Special Anodes, The Netherlands), and cathode was a graphite plate (dimensions: 4 × 4 cm). The anolyte was 50 mM PBS (pH 7) while catholyte was the synthetic wastewater prepared with ammonia chloride and tap water. The external power supply was set as 4 V (NEWARE Battery testing system 7.5.X, China).

To investigate the current response to ammonia concentration, the synthetic wastewater containing different ammonia concentrations (0–62.1 mg $NH_4^+$-N/L) was pumped into nitrification reactor first and then the effluent was fluxed with nitrogen and introduced into cathode chamber of MEC. The current was recorded by NEWARE Battery testing system 7.5.X. In order to test the effect of pH on current response to ammonia levels, pH of the synthetic wastewater was adjusted to different levels ranging from 5 to 8. Another set of experiments was performed with the goal to investigate the effect of external power supply on current response to ammonia levels. In these experiments the external voltage supplied between the anode and cathode of MEC was tested from 0.3 to 0.8 V. All the experiments were carried out in duplicate. The student's t-test was applied for statistical analysis of the results, with P-values < 0.05 were considered for significance effect on the response, while values > 0.1 indicate the variables are not significant.

### 2.2. Electrochemical analysis and calculations

Conductivity and pH were determined using a CDM 83 conductivity meter (Radiometer) and a PHM 210 pH meter (Radiometer), respectively. The concentrations of ammonia and nitrate were measured with colorimetric test kits (Spectroquant 00683, 09713; Merck, Germany). The current in the MEC circuit was monitored by NEWARE Battery testing system 7.5.X every 1 min. Q was calculated according to Q = I * t. The coulombic efficiency for nitrate removal was calculated according to the well-established mathematical formulae (Supporting information).

The results measured by biosensor were calculated by the corresponding linear equation listed in the figure. The current response was set as y value. The ammonia concentration represented as x was calculated through the equation.