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Integrated electrochemical-biological process as an alternative mean for ammonia monitoring during anaerobic digestion of organic wastes

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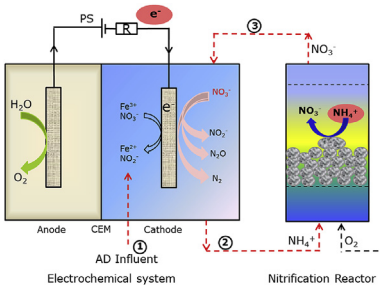
HIGHLIGHTS

- Integrated electrochemical-biological system was developed as ammonia sensor.
- Linear correlation was established between current and ammonia levels of digestate.
- Digestate pH and external voltage affected monitoring performance.
- Biosensor could exclude the interference of other electron acceptors beforehand.
- There was no significant difference compared to conventional methods in accuracy.

GRAPHICAL ABSTRACT



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ABSTRACT

Ammonia monitoring is important to control anaerobic digestion (AD) process due to inhibition effect. Here, an electrolysis cell (EC) was integrated with a complete nitrification reactor as an alternative approach for online monitoring of ammonia during AD processes. The AD effluent was pumped into nitrification reactor to convert ammonia to nitrate, followed by the introduction of nitrate-rich effluent to EC cathode. It was first evaluated with synthetic ammonia-rich digesters and was observed that the current at 5 min were linearly corresponding to the ammonia levels (from 0 to 7.5 mM NH_4^+-N, $R^2 = 0.9673$). The linear relationship was always observed regardless of different wastewater pH and external voltage. Pre-removal of other electron acceptors from digestate at cathode could eliminate their disturbances to sensor performance. Finally, the accuracy of biosensor was verified with real digestate test. The simple and reliable biosensor showed great promising for online ammonia monitoring of AD processes.

1. Introduction

Anaerobic digestion (AD), as a sustainable technology to produce biogas from various wastes such as manure, solid waste and sludge, is becoming more and more attractive across the world (Chatterjee and Mazumder, 2016; Choong et al., 2016; Rayner et al., 2017; Senghor et al., 2017). However, ammonia coming from degradation of protein in AD substrate could be an inhibitor for AD process (Angelidaki and Ahring, 1994; Hansen et al., 1998; Rajagopal et al., 2013). As reported before, low free ammonia

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concentrations (e.g. 100 mg-N L^{-1}) could inhibit an unadapted AD process (Hansen et al., 1998). Therefore, ammonia monitoring is significantly important to maintain stability of AD. Currently, the common methods to test the ammonia in aquaculture include colorimeter procedure (Nessler, phenate, and salicylate methods), ion-selective electrode for NH_4^+, and test kits relying on the Nessler or salicylate methods (Krug et al., 1979; Le and Boyd, 2012; Zhou and Boyd, 2016). However, there are still some drawbacks among these methods. Firstly, the accuracy of colorimeter methods is easily disturbed by the sample color or turbidity. Secondly, the issue of disposal of hazardous waste, which increases the complexity and operation cost, becomes a severe concern of Nessler method. Thirdly, most of the colorimetric methods need extra sample preparations (e.g., membrane filtration) which are time-consuming and costly. Lastly, the ion-selective electrode is strongly affected by the sodium and potassium although with high precision and wide detection range. New conductive materials have also been developed to monitor dissolved ammonia in water, but the synthesis of materials and sensor fabrication are still complicated and the costs are relatively high (Tao et al., 2006; Huang et al., 2016). Thus, development of an alternative environmental-friendly, simple, rapid, online and reliable ammonia sensor is in urgent need for environmental monitoring and water quality control.

On the other hand, electrochemical system has been widely applied into ammonia sensor field because of their high selectivity and sensitivity (Ribeiro et al., 2012; Herzog, 2015; Zhybak et al., 2016; Ning et al., 2017). The electrochemical ammonia sensors, which are based on the ammonia ion transfer reactions across different electrolyte interfaces, mainly include potentiometric and amperometric methods (Bertocchi et al., 1996; Abass et al., 1998; Zolotov et al., 2014; Herzog, 2015). Luo and Do (2006) reported two kinds of polyaniline-poly composite films which exhibited a high sensitivity of NH_4^+-N up to 100 mM. Ribeiro et al. (2012) also developed an amperometric sensor to detect ammonia concentrations in the range from 4.2 to 66 μM. Most of the electrochemical ammonias sensors were focused on the development of new nanomaterials or fabricating electrodes. Although with high sensitivity and selectivity, these electrochemical sensors still require tedious and complex fabrication process and high consumption of nanomaterials.

Recently, it has been demonstrated that nitrate could be successfully removed at cathode of an electrolysis cell (EC) reactor as an alternative electron acceptor (Abdallah et al., 2014; Radjenovic and Sedlak, 2015; Rajmohan et al., 2016). In biological pathway, ammonia could be aerobically oxidized to nitrate through nitrification process (Zhang et al., 2009; Samarasinghe et al., 2016; Wang et al., 2016). Therefore, coupling nitrification stage with electrochemical nitrate reduction could be a possible way to monitor ammonium during biogas production. Compared to the conventional methods and current electrochemical ammonia sensors, it may offer a fast, environmentally friendly and simple potential approach for monitoring ammonia during AD. To the best of our knowledge, such integrated system has never been explored before.

The aim of present study is to develop an alternative and potentially sustainable approach for ammonia monitoring during AD process. To achieve this goal, an integrated EC-nitrification system was constructed. In this sensor, ammonia in the AD digester was firstly oxidized to nitrate in nitrification reactor. The effluent enriched with nitrate was introduced into cathode of EC reactor for further reduction. Firstly, the sensor performance was explored with synthetic wastewater, in terms of nitrification efficiency, ammonia detection range, response time and operational stability. The effects of external power supply and pH on sensor performance were also investigated. Besides, considering other possible electron acceptors in AD digester, the digester was pumped into cathode of EC first to eliminate effects. Finally, the new sensor was tested with real AD digesters to verify its reliability. The application of this new sensor may have the potential to provide an online and reliable approach to monitor ammonia, which could be helpful to maintain AD stability.

2. Material and methods

2.1. Reactor construction and operation

An EC reactor, made of nonconductive polycarbonate plates, was a rectangular reactor composed of anode chamber (50 mL) and cathode chamber (100 mL) (Fig. 1). The electrode materials were a titanium woven wire mesh (4 × 5 cm, 0.15 mm aperture, William Gregor Limited, London, UK) coated with 0.5 mg cm^{-2} Pt for cathode, and 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, BA Schiedam, Netherlands) for anode. The anode chamber was filled with 50 mM PBS (pH-7) and cathode chamber was filled with synthetic wastewater. The synthetic wastewater was prepared with ammonia chloride being dissolved into tap water at different ammonia levels. Two chambers were separated by a cation exchange membrane (CEM, CMI 7000, Membrane international, NJ, USA). The rubber gaskets and screws were used to avoid leakage during the assembling. The membrane was put in 50 mM NaCl solution for 24 h, and then soaked in distilled water until use. A power supply (NEWARE Battery testing system 7.5. X, Shenzhen, China) was used to provide the external voltage to the reactor. During the study of influence of other electron acceptors on sensor performance, an anion membrane (AEM) was used to avoid NH_4^+ migration.

A lab-scale nitrification reactor was set up to complete the oxidation from ammonia to nitrate. A glass bottle (500 mL) was used for the reactor, and the effluent of a membrane bio-reactor (MBR) was used as the inoculum to set up this nitrification stage. The characteristics of inoculum were 2.5 g L^{-1} (total solid content) and pH 7.04. During the enrichment of nitrification bacteria, the medium, which contained 2.45 g L^{-1} NaH_2PO_4, 4.58 g L^{-1} Na_2HPO_4, 0.1 g L^{-1} KCl, 0.1 g L^{-1} $MgCl_2 \cdot 6H_2O$, 0.1 g L^{-1} $CaCl_2 \cdot 2H_2O$, 12.5 mL L^{-1} mineral solution and vitamin solution as describe before, was used. $NaHCO_3$ (2 g L^{-1}) was used as the carbon source and electron donor. The aeration was obtained directly from the air as it was open to air and the solution was fully mixed by magnetic stirrer.

2.2. Experimental design

In the investigation of linear relationship between current and ammonia concentration, the synthetic wastewater with different ammonia levels (0–7.5 mM NH_4^+-N) was pumped into nitrification reactor first and then the effluent was purged with nitrogen and introduced into cathode chamber of EC. The current in circuit was recorded by NEWARE Battery testing system 7.5. X (NEWARE, Shenzhen, China). In one set of tests, the external voltage was set at 1.5 V, 1.8 V, 2 V and 2.3 V to elucidate the effect of external power on sensor performance. Then the effect of nitrification effluent pH on sensor performance was studied at four different pH levels (pH 4, 6, 7 and 8). Subsequently, the pretreatment of sensor was evaluated by adding 21.4 μM Fe^{3+} and 714.3 μM NO_3^- to the synthetic wastewater, respectively. To verify the accuracy of sensor, it was tested with two real AD effluents. One was collected from a lab-scale AD reactor for biogas upgrading which was operated at 37 °C (noted as AD effluent 1). The other one was taken from a thermophilic lab-scale AD reactor fed with manure (55 °C) (noted as AD effluent 2). All experiments were carried out in duplicate at room temperature.