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Electrochemical monitoring of ammonia during anaerobic digestion

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Abstract

Ammonia is known as key inhibitor to methanogens in anaerobic digestion (AD) process. It's of importance to develop efficient tool for ammonia monitoring. In this study, an electrolysis cell (EC) coupled with a complete nitrification reactor was developed as sensor for real time and online monitoring of ammonia in AD. The AD effluent was pumped into nitrification reactor first, in which ammonia was converted to nitrate. Afterwards, the nitrate-rich effluent was introduced into cathode chamber of EC. The correlation between currents and ammonia levels was first evaluated with synthetic ammonia-rich digesters. It was observed that the initial transient currents (0 min) were linearly corresponding to the ammonia levels (from 0 to 95.75 mg/L NH_4^+-N, R^2 = 0.9673). Finally, this new sensor was tested with real AD effluent and the results showed no significant difference with that measured by conventional methods. The sensor developed here has great potential for online, cost-saving, fast and accurate ammonia monitoring in AD process

Keywords

Anaerobic digestion; ammonia; electrolysis cell; transient current

INTRODUCTION

Ammonia as a notorious environmental pollutant is toxic to the methanogens in anaerobic digestion (AD) when the ammonia level exceeds over 1.5 g NH_4^+-N/L (Wang et al. 2016, Zhang and Angelidaki 2015). Thus, it's important to monitor the ammonia level in order to better control of AD process. The traditional methods to test ammonia include titration, colorimetry, gas phase molecular absorption spectrometry and spectrophotometry with salicylic acid etc. However, most of these methods are expensive, not real time testing, offline and causing secondary pollution etc. Therefore, it's in urgent need to develop a real time and online sensor for ammonia level in AD.

It has been reported that nitrate could be used as the electron acceptor in the cathode of EC. Thus, linear relationship between current and nitrate concentration could be established. Furthermore, considering that the ammonia could be oxidized to nitrate in nitrification stage. A final correlation between ammonia concentration and current could be established. In this study, an innovative ammonia sensor which integrated EC and nitrification process was developed. The feasibility of the sensor was first verified with synthetic wastewater. Finally, the sensor was tested with real AD waste to demonstrate it applicability.

MATERILA AND METHODS

Sensor configuration 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). The cathode electrode was a titanium woven wire mesh (4×5 cm, 0.15 mm aperture, William Gregor Limited, London) coated with 0.5 mg/cm^2 Pt. The anode used

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). The anode chamber was filled with 50 mM PBS (pH 7) and cathode chamber was filled with tested ammonia-contained tap water. Two chambers were separated by a cation exchange membrane (CEM, CMI 7000, Membrane international, NJ). To activate a complete nitrification process, a beaker with 500 mL was used as the nitrification reactor. The effluent of a membrane bio-reactor (MBR) was used as the inoculum to set up this nitrification stage.

To investigate the relationship between current and ammonia levels, the tap water contained different ammonia levels (0-95.75 mg/L) was introduced into nitrification first and then effluent was pumped into cathode chamber of EC sensor. The current was recorded by NEWARE Battery testing system 7.5.X (China). All the experiments were done in duplicate. To check the difference between two series of values, the student's t-test was conducted to do the statistical analysis and P-values<0.05 were chosen to have significance effect on the response, while values>0.1 indicate the variables are not significant.

Electrochemical analysis and calculations

The pH and conductivity of tested solution were measured by and a PHM 210 pH meter (Radiometer) and a CDM 83 conductivity meter (Radiometer), respectively. The ammonia testing kit was used to test the ammonia level. The current was recorded by NEWARE Battery testing system 7.5.X every 1 minute, and external power supply was offered by Machine A as well. Q was calculated with the equation of Q=I * t.

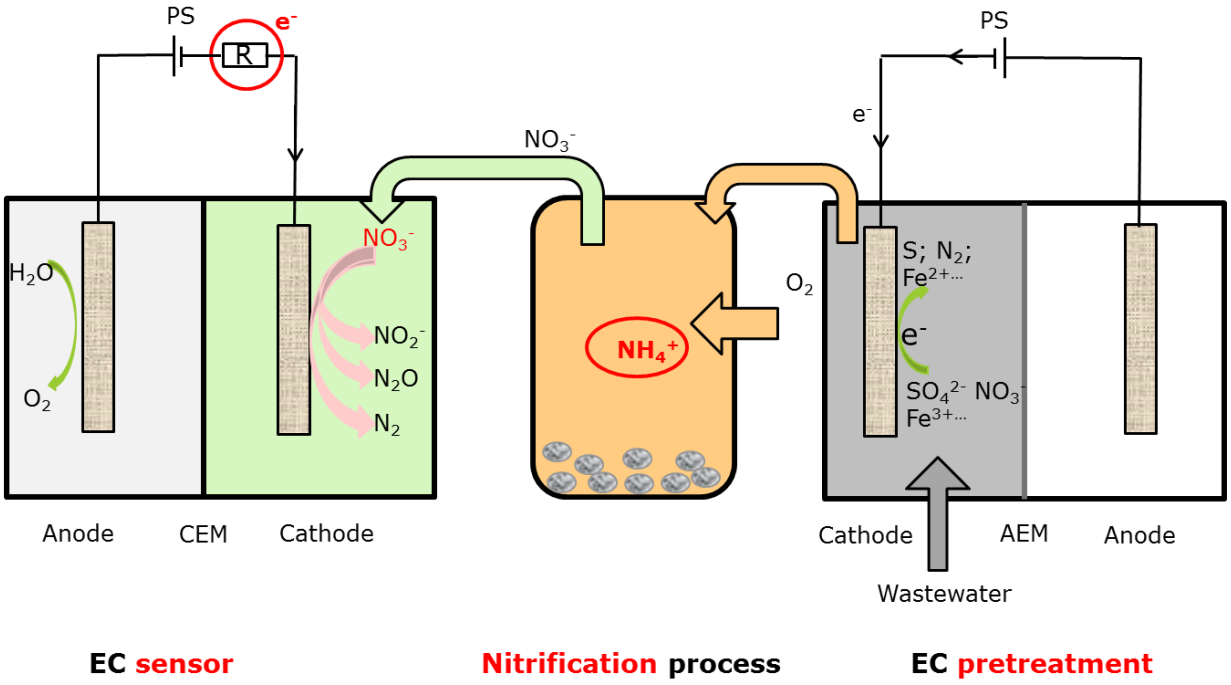

Figure 1. Schematic diagram of EC sensor, nitrification reactor and EC pretreatment.

CEM: the cation exchange membrane. AEM: the anion exchange membrane.

RESULTS AND DISCUSSION

Nitrification stage

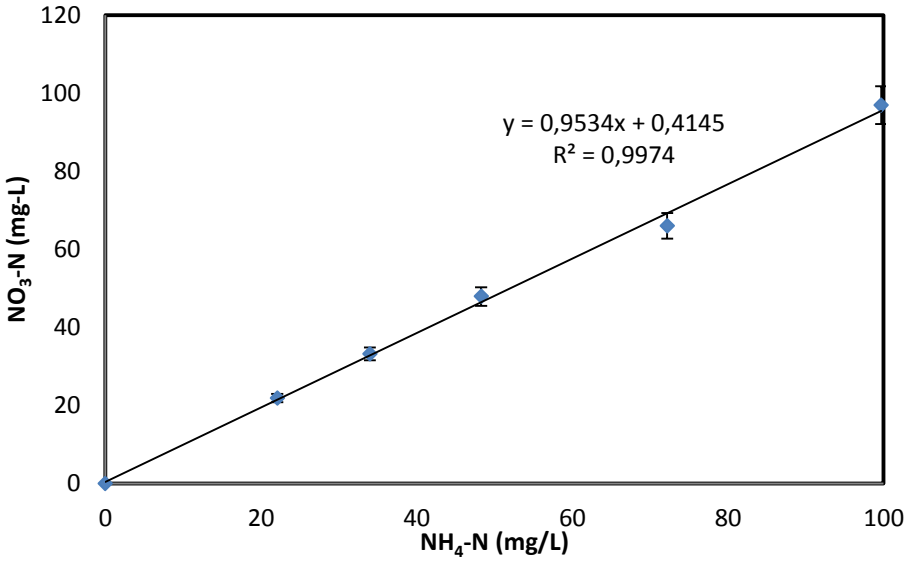

Figure 2. The correlation between nitrate and ammonia concentration after denitrification process

Fig.2 depicts the nitrification stage before EC sensor. As shown in Fig.2, a complete nitrification process was achieved in this study. All the nitrifying process was finished in four hours. There's a good linear relationship between the ammonia level and nitrate concentration when the ammonia changed from 0 to 95.75 mg/L (R^2=0.9974). The high and stable conversion efficiency provided the insurance of first step of ammonia oxidized to nitrate.

Sensor performance

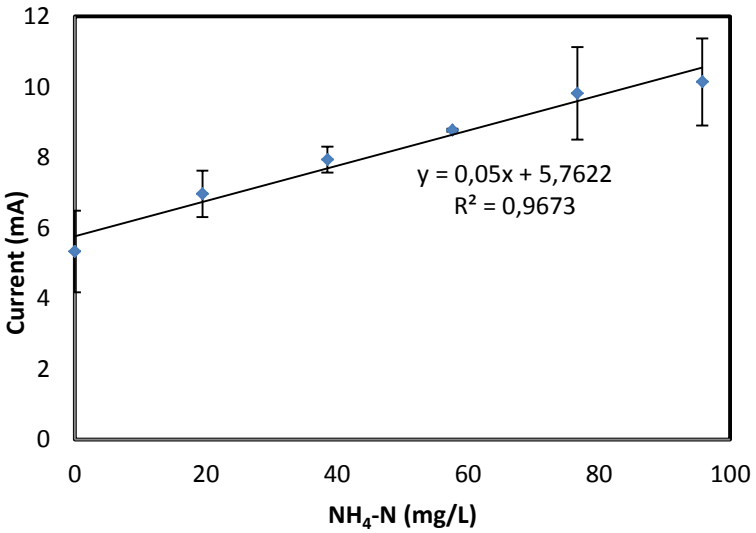

Figure 3. Linear relationship between current and ammonia levels at external voltage-1.8V and solution pH-6.

The correlation between instant current (at time 0h) and ammonia level was established as shown in Figure 3. The current linearly increased with ammonia levels from 0 to 95.75 mg/L NH_4^+-N (5.33 to 10.14 mA, R^2= 0.9673). The different momentary current was related to the different NO_3^--N concentrations in cathode chamber. The current at 0 mg/L NH_4^+-N is 5.33 mA, which could be seen as the background value. This current came from the other possible electron acceptors (i.e., SO_4^{2-}) in the tap water. As the NH_4^+-N level increasing, the NO_3^--N increased as well. The more electron acceptors, the more electrons flowed through the circuit, which is demonstrated by the increasing current. The above results indicate the feasibility of this sensor for online monitoring ammonia.

Application in real AD effluent

Table 1. Determination of ammonia levels in real AD digesters by EC sensor and testing kits

sample	NH_4^+-N (measured by kit)	NH_4^+-N (measured by sensor)	pH	Conducitivity (us/cm)
AD effluent 1	1542	1647,8	8.87	1690

The EC new sensor was tested with real AD effluent to verify the applicability. The sample was taken from three lab-scale AD reactors. The results of ammonia concentrations tested by kits and EC sensor were summarized in Table 1 along with the characteristics of sample. The above results showed the results tested by EC sensor were close to the results by tested by kits. Anova analysis showed no significant difference ($P<0.05$) between these two series of values which demonstrated the accuracy of this new sensor.

CONCLUSIONS

It was observed that the sensor responded immediately to the NH_4^+-N levels without any lag phase. This convenient, simple, real time and reliable sensor had a great promising potential in ammonia monitoring of AD digesters.

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