

ORIGINAL ARTICLE

Performance of Self-Manufactured Ion Selective Microelectrode (ISME) for Continuous Monitoring of Ammonia and Nitrate Ions

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Abstract

The ion selective microelectrodes (ISME) have been applied to observe the continuous profiles of NO₃-N and NH₄-N in bulk solutions or biofilms. In order to evaluate the performance and applicability of ion concentration measuring system, the characteristics, such as slope of calibration curve, detection limit and potentiometric selectivity coefficient were investigated. The slopes of calibration curve showed high degree of correspondence for each target ion concentrations. And the detection limits of nitrate and ammonia ion selective microelectrode were 10-4.7 M and 10-4.4 M, respectively. These ion selective microelectrodes were proved that their own performance could be maintained for 16 days after making. NO₃-N and NH₄-N selective microelectrodes were also adapted to detect the continuous ion profiles of cilia media packed MLE (Modified Ludzack-Ettinger) process. And the monitored nitrate and ammonia ion profiles with the ion selective microelectrode were stable and well corresponded to the results with conventional ion chromatograph. However, the electric potential was unstable until 8 hr because of the unknown noise. The tip shape and performance of the ion selective microelectrode was stably kept over 2 days continuous monitoring.

Key words : Ion Selective Microelectrode, Ammonium ion, Nitrate ion, Continuous monitoring, Potentiometric selectivity coefficient

1. Introduction.

Nitrogen and phosphorous are classified as a macro nutrient and widely distributed in the natural. However, these nutrients should be properly removed from wastewater because these components are well known as eutrophication and red tide inducing materials. The biological nutrient removal (BNR) process is prevalent treatment technology to remove nutrients in domestic and industrial wastewater (Gálvez et al., 2003; Fikret and Ahmet, 2003; Rustrian et al., 1999).

There are two steps in nitrogen removal process. At first step, nitrification, NH₄-N is transforms into

NO₃-N. The NO₃-N changes to nitrogen gas in the second step denitrification. It is well known that theoretically 3.7 g COD is needed to remove 1 g nitrate (Henze, 1991). However, the C/N (COD/Nitrogen) ratios of domestic wastewater in Korea are very low with below 3.7. Therefore, external carbon source is essentially demanded to remove nitrogen. The decision of dosing amount of external carbon source is very important to avoid organic over loading for BNR processes and to achieve proper removal of nitrogen in wastewater. However, it is very difficult to optimize the dosing amount of external carbon source proportionally to C/N ratio of wastewater because the C/N ratio of wastewater is

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continuously changed in real plants (Park et al., 2004).

To optimize the dosing amount of external carbon source, realtime monitoring of nitrogen compounds such as nitrate and ammonia ion in the wastewater is needed. The characteristics of ion selective microelectrode (ISME) are short response time and direct measurement. Therefore, realtime measurements of ion compounds with ISME could give essential information for optimizing the dosing amount of external carbon source.

In this study, we have manufactured nitrate and ammonia ion selective microelectrode (ISME) and build up the ISE system. The self manufactured ISMEs were made survey on the point of the ISME performance, stability, detection limit and durability to evaluate the applicability to real BNR processes.

2. Materials and Methods

2.1. Fabrication of ion selective microelectrode

In this study, NH_4^+ and NO_3^- ion selective microelectrodes were fabricated using by liquid ion exchanger membrane. Fabrication procedures are as follows; (debeer, 1991, 1993; Sweerts et al.; 1989; Li, 2001)

(1) Pulling & Tip formation: Glass capillary tube was pulled until the diameter range is under $1\mu\text{m}$. Then tip was sharpening to have wider tip surface and to extend the contact surface with beveller (BV-10, Sutter Instrument Co.)

(2) Silanization: Kept in the oven at 150°C 3 hrs. After removing of remaining water in glass capillary tube, silanizing agent (N, N - dimethyltrimethylsilylamine) was filled in the tip to form a hydrophobic surface. Then, keep in the oven at 200°C overnight.

(3) Filling with electrolyte: Ammonium microelectrode was filled with 0.05 M KCl and nitrate microelectrode was filled with mixture of 0.05 M KCl and 0.05 M KNO_3 .

(4) Filling with sensor cocktail: To form the ion

selective membrane having selectivity to the target ion, microelectrode was filled with sensor cocktail. (NH_4^+ : Ammonium Ionophore I cocktail A, NO_3^- : Nitrate Ionophore I cocktail A)

(5) Tip coating: Tip was coated with 1 mL of protein solution to increase the tip's strength and form the protein membrane. The protein solution is the mixture of 100 mg BAS (bovine serum albumin), $900\mu\text{l}$ 50 mM sodium phosphate and $10\mu\text{l}$ of 25% glutaraldehyde.

2.2. Characteristics of fabricated ion selective microelectrode

Calibration curves were calculated using standard solution range in $10^{-2}\sim 10^{-6}$ M to estimate the relationship between concentration of target ion and electromotive force (EMF). (Li, 2001; Miller, 1995) Potentiometric selectivity coefficient of ion selective microelectrode was defined as the ability of ion-selective microelectrode to distinguish the ions. The selectivity coefficient, $K_{A,B}^{\text{pot}}$ is evaluated by means of EMF of the ion-selective microelectrode in mixed solutions of the target ion and interfering ion. (Richard and Erno, 1994)

$$K_{A,B}^{\text{pot}} = (a_A/a_B)^{Z_A/Z_B}$$

Where $K_{A,B}^{\text{pot}}$ is the selectivity coefficient, a_A is the target ion activity, a_B is the interfering ion activity, Z_A is the target ion charge, Z_B is the ion activity.

2.3. Monitoring of ion compounds in cilia media packed MLE reactor with ISME

Fig. 1 shows the lab scale cilia media packed MLE (Modified Ludzack-Ettinger). The reactor consists of two mixed activated sludge processes and a sedimentation tank. The anoxic basin for denitrification was equipped with stirrer. The aerobic basin for nitrification and organism biodegradation was equipped with ion selective microelectrode to measurement the ammonium and nitrate. The hydraulic retention time (HRT) was

set at 4h. During the experiments, the influent of reactor was synthetic wastewater which containing 200 mg/L COD, 40 mg/L NH_4^+ -N and trace elements. The components of synthetic wastewater is shown in Table 1.

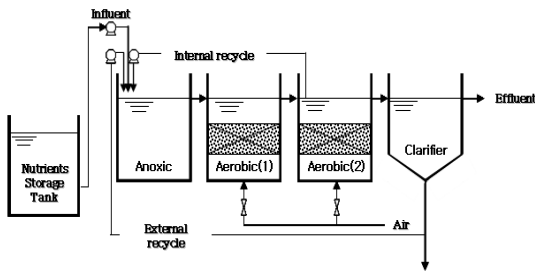


Fig. 1. Schematic diagram of cilia media packed MLE reactor.

Table 1. Synthetic wastewater components

components	wastewater	
	g/100L	
Glucose	21	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ 1.75
Yeast Extract	0.5	NaCl 3.75
NH_4Cl	15.3	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 1.25
KH_2PO_4	2.19	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 0.0125
NaHCO_3	45	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ 0.00558
KCl	1.75	$\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ 0.00055

3. Results and Discussion

3.1. Calibration curves and detection limits

The potential difference between ion-selective microelectrode and reference electrode were measured, and then we could estimate the concentration of target ion. The relationship between concentration and electromotive were calculated by the Nernst equation. The theoretical electromotive force (EMF) is given by the Nernst equation:

$$E = E^0 + (RT/nF) \cdot \log(a)$$

Where, E is electromotive force (mV), E^0 is reference potential (mV), R is the Gas constant (8.314 joules/K·mole), T is the absolute temperature (K), n is the charge on the ion, F is the Faraday constant (96,485 coulombs/mol) and $\log(a)$ is the logarithm of the activity of measured ion. Calibration curves were calculated using standard solution range in 10^{-2} ~ 10^{-6} M to estimate the relationship between concentration of target ion and electro motive force (EMF). The Calibration curve of NH_4^+ and NO_3^- microelectrode were shown in Fig. 2. Concentration of the target ion is proportional to response signal of electrode. The average calibration curve of ion selective microelectrode is about 48 mV. Also, the detection limit of ion selective microelectrode is is

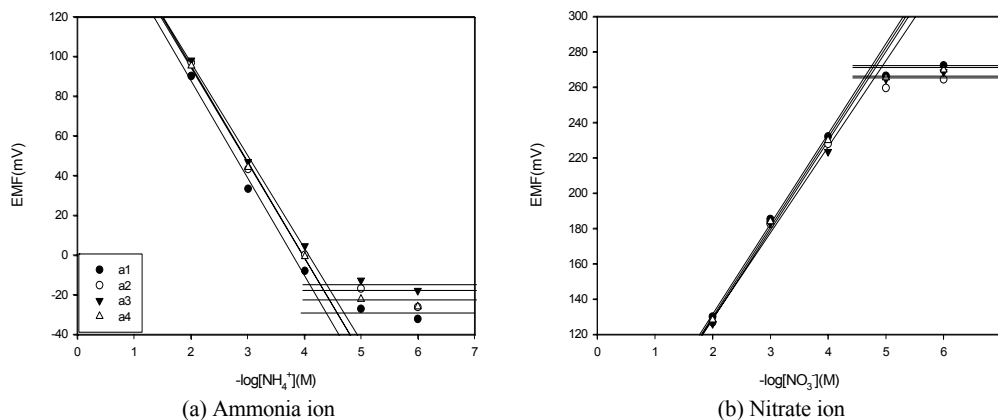


Fig. 2. Calibration curves of ion selective microelectrodes.

higher than 10^{-4} M. Therefore, the fabricated ion selective microelectrode could measure the target ion concentration in the wastewater.

3.2. Variation of ammonia and nitrate ion microelectrode calibration curves according to elapsed time

To check the reproducibility of microelectrode, calibration curves and correlation coefficients were observed according to time. Fig. 3 showed that variation of NH_4^+ and NO_3^- microelectrode response according to the elapsed time. The fabricated ion selective microelectrodes were kept in conditioning solution. The observed responses have no change for 16 days. The slope of calibration curves decreased from 48 mV to 45 mV for 16 days. Also, y-intercept reduced a little. It seems to be caused by the transformation of membrane of ion-selective microelectrode. So the fabricated ion selective microelectrode is in needs of a calibration not only before but also after measurement.

3.3. Potentiometric selectivity coefficient to interfering ions

The effects of interfering ions were evaluated by FIM method (Lochard and Ernö, 1994). The interfering ions of ammonium ion selective microelectrode are

glucose (200 mg/L), K^+ (4 mM), Na^+ (4 mM), Mg^{2+} (4 mM) and Ca^{2+} (4 mM). The interfering ions of nitrate ion selective microelectrode are glucose (200 mg/L), NO_2^- (4 mM), Cl^- (4 mM), SO_4^{2-} (4 mM) and HPO_4^{2-} (4 mM). In case of adding glucose to solution, there were little changes. The potentiometric selectivity coefficients of ammonium and nitrate ion to interfering ions are shown in Table 2.

Based on these results, it means that interfering ions seldom have an effect on the potentiometric selectivity coefficient. It showed that selectivity to target ions is 100 times higher than interfering ions except for nitrite ion.

Table 2. The potentiometric selectivity coefficient of ammonia and nitrate ion

Target ion	interfering ions	$K^{\text{pot}}_{A, B}$	Target ion	interfering ions	$K^{\text{pot}}_{A, B}$
NH_4^+	K^+	0.0028	NO_3^-	NO_2^-	0.0396
NH_4^+	Na^+	0.0013	NO_3^-	Cl^-	0.00007
NH_4^+	Mg^{2+}	0.00004	NO_3^-	SO_4^{2-}	0.0004
NH_4^+	Ca^{2+}	0.00007	NO_3^-	HPO_4^{2-}	0.0003

3.4. Evaluation of continuous monitoring with ion selective microelectrode

Fig. 4 shows the continuous profiles of ammonium and nitrate ion measured by ion selective microelectrode

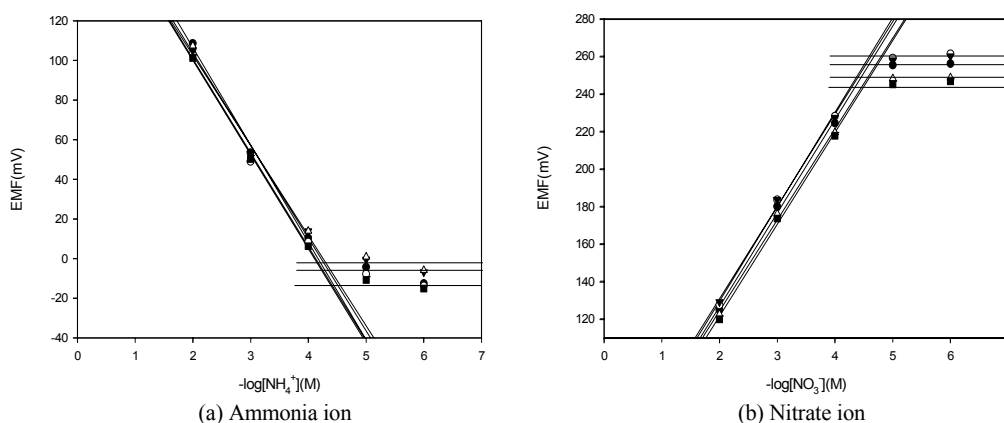


Fig. 3. Variation of microelectrode calibration curves according to elapsed time; 4 days (\circ), 7 days (\blacktriangledown), 10 days (\bullet), 13 days (\triangle), 16 days (\blacksquare).

in the cilia media packed MLE process. The concentrations of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ were measured using by ion selective microelectrode for 8, 12, 48 hours. The measured values by ion selective microelectrode were compared by the results of analyses by AA3 (Auto Analyzer III) and Ion chromatography instrument. Error ranges of measured values were $5\pm 5\%$. The electric potentials were unstable for 8 hours. Therefore, it seems that ion selective microelectrode needs a time for stabilization to get a correct value. It seems to be caused by noise. (Jensen et al., 1993)

No damages in microelectrode tip were observed after continuous monitoring with ISME and the performance was also maintained after monitoring. Furthermore, the microelectrode showed stable capacity of measurement during additional 2 days. Based on these results, it is considered that ion selectivity microelectrode is appropriate monitoring tool for ion compounds such as $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$.

4. Conclusions

The self manufactured nitrate and ammonia ion selective microelectrodes (ISMEs) were characterized to evaluate their performance and following conclusions were obtained.

1) Although there are some differences between slope of calibration curve in standard solution and

theoretical value according to the Nernst equation, concentration of target ion is proportional to response signal of electrode. Average detection limit of ammonia and nitrate microelectrode are lower than $10^{-4.4}$ M and $10^{-4.7}$ M, respectively. The fabricated ion selective microelectrode could be used measure the various ions concentration in the wastewater.

2) The self made nitrate and ammonia ISE were proved that their own performance could be stably maintained for 16 days after making.

3) The interfering ion effects were also not significance problem for the potentiometric selectivity coefficient of these ISME. It showed that selectivity to the target ions is 100 times than interfering ions except for nitrite ion.

4) The continuous nitrate and ammonia ion monitoring in cilia media packed MLE process was well corresponded to the analysis results with ion chromatograph. $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ selective microelectrodes were also adapted to detect the continuous ion profiles of cilia media packed MLE process. And the tip shape and performance of the ion selective microelectrode was stably kept over 2 days continuous monitoring.

Therefore, it is considered that ion selectivity microelectrode could be effective continuous monitoring tool for ion compounds in the wastewater treatment systems.

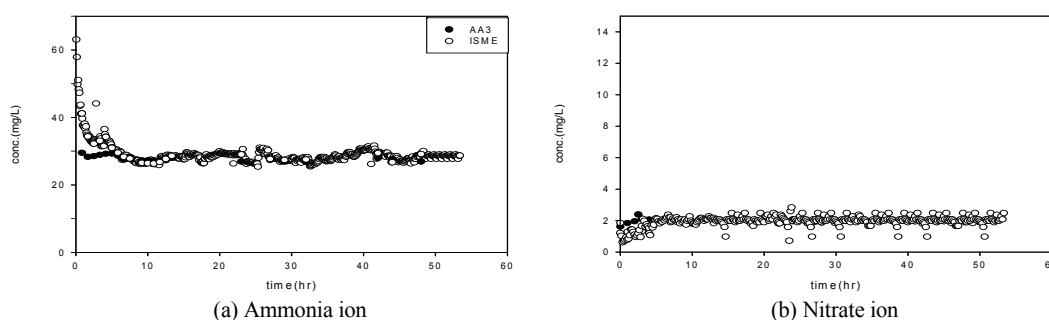


Fig. 4. Variation of microelectrode calibration curve for 2 days.

Acknowledgements

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