Int. J. Plasma Environ. Sci. Technol. 15 (2021) e02001 (9pp)

International Journal of
Plasma Environmental Science and Technology

Regular Paper

DOI: 10.34343/ijpest.2021.15.e02001

Combined of dielectric barrier discharge and electrolysis methods to generate nitrogen compounds in aqueous solution from room air

Yoshihiro Kawada[*], Hiroto Endo, Hiroki Yamanaka, Hirotaka Shimizu

Electrical Environmental Energy Engineering Unit, Polytechnic University of Japan, Japan

* Corresponding author: kawada@uitec.ac.jp (Yoshihiro Kawada)

Received: 15 March 2021
Revised: 26 April 2021
Accepted: 12 May 2021

Abstract

Hydroponics is the process of growing plants without soil medium in an aqueous solution containing the required nutrients. For this technique, phosphorus, potassium, and nitrogen fertilizers are added to the water. Nitrogen gas in the atmosphere cannot be absorbed directly by plants, and the nitrogen must be transformed into nitrate, nitrite, and ammonia for uptake by plants. Previous research has shown that dielectric barrier discharge products from air affect plant growth. Only nitrogen oxides are produced from electric discharge in air, and the aqueous solution of nitrogen oxide is nitric acid, which has low pH. Therefore, pH adjustment is necessary for hydroponics. In this study, electric discharge products were dissolved in water, and then, the solution was kept for 24 h as ozone was degassed. Subsequently, nitrate was reduced by electrolysis. In this study, the pH of the solution containing the electric discharge products was increased to 5.5 or more. Our past research had shown that the pH can be increased by using a metal electrode and electrolysis; however, metal ions are dissolved by electrolysis. In this study, a graphite electrode was used; additionally, the electrolyte was separated using a dialysis membrane, and the area of the cathode electrode was increased. The stirring bar was set under the cathode electrode. These methods were tested to evaluate the effect on electrolysis and rising the pH.

Keywords: Ozone, electrolysis, nitrate, nitrite, ammonia.

---

1. Introduction

Hydroponics can be adopted in a plant factory. This technique requires solution fertilizer, with phosphorus, potassium, and nitrogen fertilizer as the main components. Nitrogen fertilizer is mainly composed of nitrate nitrogen (nitrate ion), nitrite nitrogen (nitrite ion) and ammonia nitrogen (ammonium ion). Although the atmosphere contains 78% nitrogen, it cannot be used as a direct source of nitrogen fertilizer; nitrogen has to be converted into nitrogen oxides and ammonia for uptake by plants.

In hydroponics, the solution is aerated for supplying sufficient oxygen to the roots. This study was motivated by the fact that ozone can be used for both sterilization and deodorization; further, ozone and nitrogen oxides can be produced by barrier discharge with room air [1, 2]. Barrier discharge products in aqueous solution are known to affect plant growth [3–5]. However, when nitrogen oxides are dissolved in an aqueous solution, the pH of the solution decreases [5, 6]. Hence, pH adjustment is necessary. For example, watercress grown in a hydroponic system requires a near-neutral aqueous solution with a pH of 5.5 or higher.

Nitric acid electrolysis is performed to treat wastewater; for example, such treatments are adopted for domestic wastewater and agricultural water [7, 8]. Furthermore, the reduction efficiency of such an electrolysis system is improved by using an electrode with a diamond-doped electrode for a wide potential window [9]. In addition to the Haber–Bosch method, methods for producing ammonia at temperatures close to normal temperature and pressure, such as ammonia generation with nonthermal plasma techniques, have been studied [10, 11].

In this study, the nitrogen oxide solution is reduced by electrolysis. However, if a metal electrode was used, it would have dissolved in the solution during electrolysis. Therefore, graphite electrodes were used for electrolysis to prevent dissolution. In addition, various conditions were tested—a dialysis membrane was used to separate the anode and cathode tanks, the cathode electrode area was increased, and the cathode tank was agitated during electrolysis to realize a pH greater than 5.5. The techniques were tested, and the nitrate and ammonia concentration and pH were measured and evaluated to identify effective techniques to increase the pH of the solution.

2. Methods

2.1 Bubbling air treatment with barrier discharge reactor

The diagram of pretreatment system is shown in Fig. 1. Ozone-laden gas was generated with a barrier discharge. Distilled water (300 mL) was bubbled with ozone-laden gas in a gas-washing bottle. The barrier discharge system is shown in Fig. 1. A stainless-steel coil spring (wire diameter 0.7 mm, outer coil diameter 7 mm, and number of turns 40) was placed in the glass tube (inner diameter 8 mm and thickness 1 mm), and aluminum foil was wrapped on the outside of the glass tube. A high-voltage power supply (Chuen Denshi Kogyo, HPS 005-100) was used to apply a sinusoidal wave AC high voltage (4 kV_{pp}, 13.9 kHz) on the stainless-steel coil spring, and the aluminum foil was ground, and then a dielectric barrier discharge was generated. The room air was adjusted to a flow rate of 0.9 L min^{-1} through the glass tube; then, the ozone concentration was 550-650 ppm.

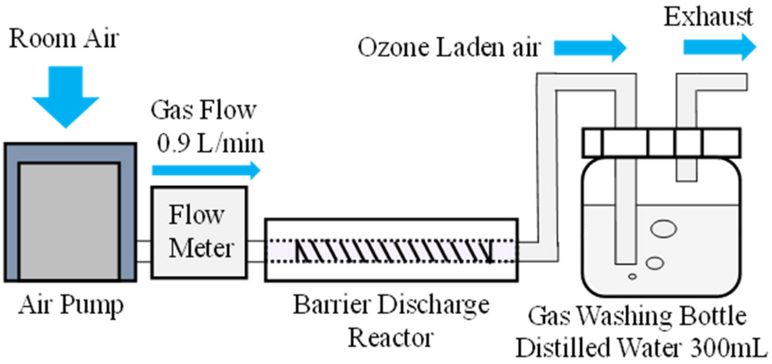
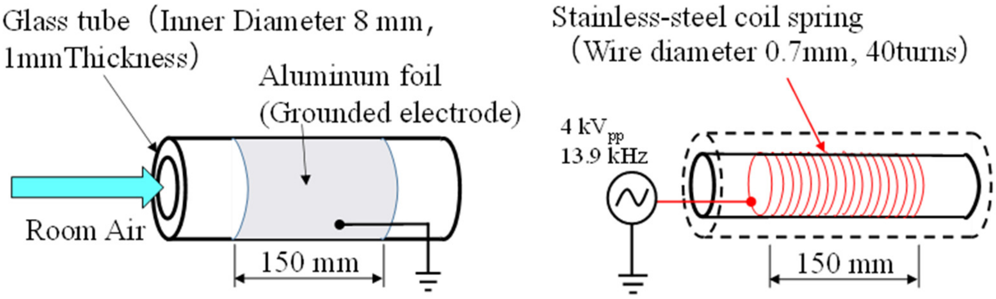


Fig. 1. Experimental apparatus of dielectric barrier discharge reactor and water treatment.



(a) External structure (b) Internal structure

Fig. 2. Schematic of the barrier discharge reactor.

2.2 Treatment with electrolysis

The electrolysis system for the bubbling treatment solution is shown in Fig. 3. An electrolytic cell (Shimadzu Rika, DB-20) was filled with pretreatment water (200 mL), and then, electrolysis was performed for 3 h. A DC power supply (Yokogawa, GS610 Source-measure unit) was used to apply positive dc 10–50 V to the anode electrode. The basic electrode was the graphite plate (10-mm width and 2-mm thickness), and the wide electrode had a width of 30 mm. The dialysis membrane was mainly composed of cellulose, and a molecular weight cut-off of this membrane has about 12000–14000. Hence, for the pretreatment solution, degassing of ozone is necessary. However, the degassing process may be easily executed by changing the dialysis membrane to a ceramic filter in the future. The dialysis membrane was set near the cathode electrode; therefore, the anode and cathode tank capacities were 115 and 85 ml, respectively. A magnetic stir bar (length 20 mm and diameter 7 mm) was placed under the cathode electrode in the tank. Therefore, the cathode electrode area was decreased by using the magnetic stirrer.

The pH of the solution was measured using a pH meter (Horiba Ltd., D-75). The dissolved concentrations of ozone, nitrite, nitrate, and ammonia were measured using Multiparameter Benchtop Photometer (Hanna Instruments, HI-83300). Due to using this instrument, the unit of nitrate concentration in this paper is "mg L^{-1} (as NO_3^--N)", the unit of nitrite concentration is "mg L^{-1} (as NO_2^--N)" or "mg L^{-1} (as NO_2^-)", and the unit of ammonia concentration is "mg L^{-1} (as NH_3-N)". In addition, during nitrate and nitrite measurement, a strong oxidizing agent may interfere with the measurement. Although ozone was reduced to the maximum extent possible before the experiment, its effect on the measurement could not be evaluated.

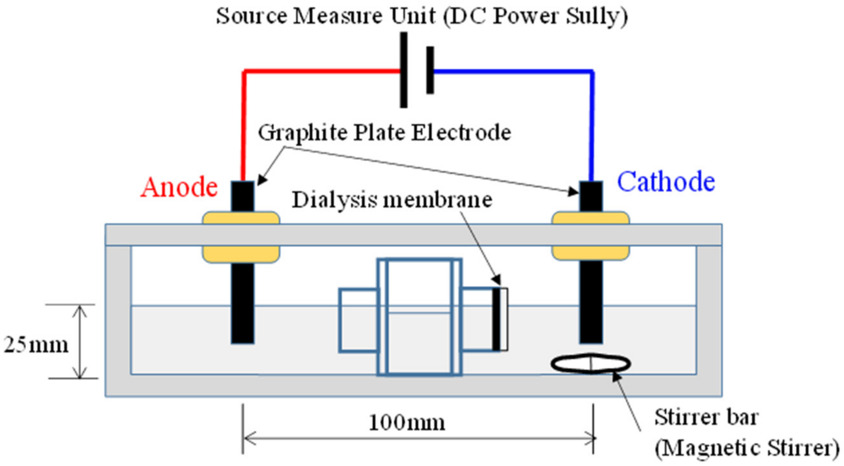


Fig. 3. Experimental apparatus for electrolysis.

3. Results and discussion

3.1 Ozone bubbling and stop time

Pretreatment was performed for 3 h to obtain a solution with nitrate ion concentration >100 mg L^{-1}. The pH of this solution was 2.8. For ensuring dissolved ozone reduction and the stability of nitrate ion concentration, the pretreatment solution was kept for a long time at room temperature.

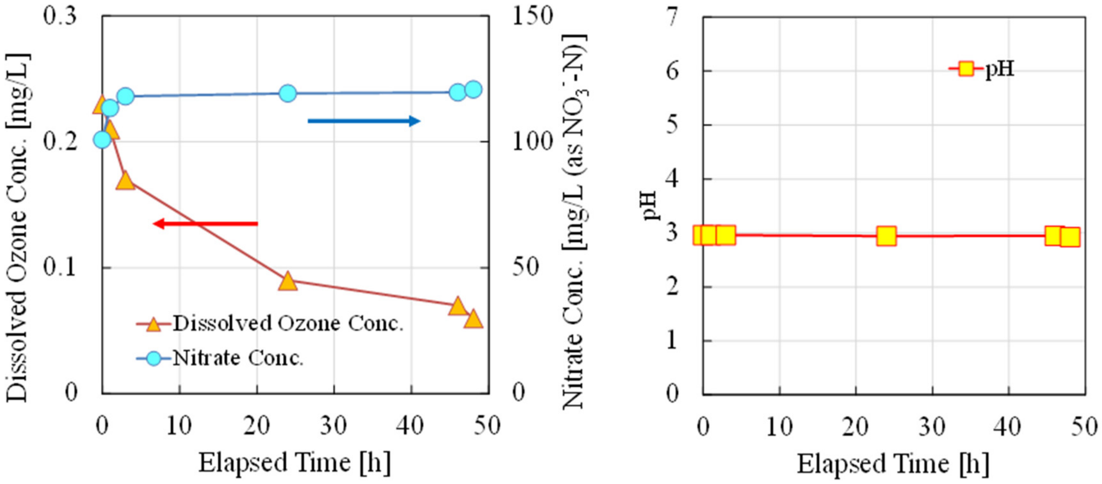


Fig. 4. Time dependencies of the dissolved ozone and nitrate concentrations and pH.

The time dependencies of the pH and nitrate concentration are shown in Fig. 4. Especially 24 h after the start for elapsed time, the nitrate concentration increased as the ozone concentration decreases. It is probable that the nitrogen oxides retained in the gas phase of the gas washing bottle were dissolved, or dissolved ozone was released into the air and became nitrogen oxides, dissolved again. In this study, the elapsed time was 24 h, considering the time needed to reduce ozone concentration. The pH of the solution remained constant for 48 h.

3.2 Electrolysis under a basic condition

The reactions occurring during electrolysis are shown in Equations (1)–(5) [7]. Water is electrolyzed at the cathode electrode, generating H_2 and OH^-. The reaction producing nitrite from nitric acid is given in Equation (2), and production of ammonia from nitrite is shown in Equations (3)–(5). In particular, both equations represent reactions in which electrons are donated, and it is thought that the reaction proceeds at the cathode.

$$H_2O + e^- \leftrightarrow 1/2H_2 + OH \qquad (1)$$

$$NO_3^- + H_2O + 2e^- \leftrightarrow NO_2^- + 2OH^- \qquad (2)$$

$$NO_2^- + 5H_2O + 6e^- \leftrightarrow NH_3 + 7OH^- \qquad (3)$$

$$NO_2^- + 7H^+ + 6e^- \leftrightarrow NH_3 + 2H_2O \qquad (4)$$

$$NO_2^- + 8H^+ + 6e^- \leftrightarrow NH_4^+ + 2H_2O \qquad (5)$$

The bubbling treated solution without a dialysis membrane and stirring bar was electrolyzed for 3 h. The anode and cathode areas were 548 mm^2 each. The current and applied voltage is shown in Fig. 5, and the charge during the electrolysis for the operating time is shown in Fig. 6. The current was proportional to applied voltage. The changes in the pH for the application of 50 V for 3 h are shown in Fig. 7. Although charge flows into the electrolyte for 3 h, the pH remains constant. In a uniform electrolyte, even if nitrate (NO_3^-) is reduced to nitrite (NO_2^-) at the cathode, nitrite (NO_2^-) is oxidized to nitrate (NO_3^-) at the anode, as shown in Equation (2). If such a reaction occurs repeatedly, reduction to NH_3 does not proceed. Therefore, the effect of divided the electrolyte into anode and cathode tanks was tested.

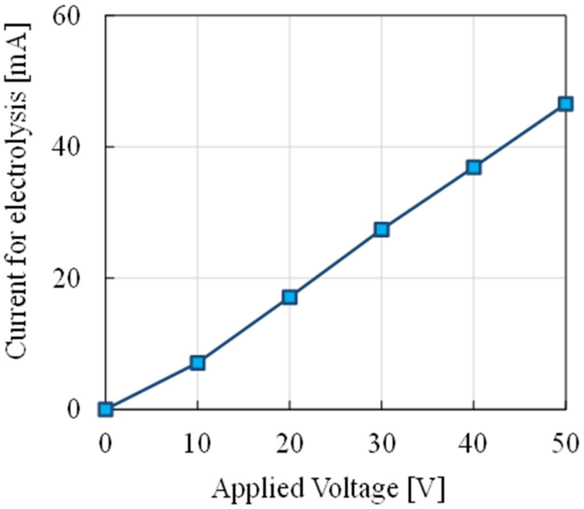


Fig. 5. Experimental apparatus for the dielectric barrier discharge treatment.

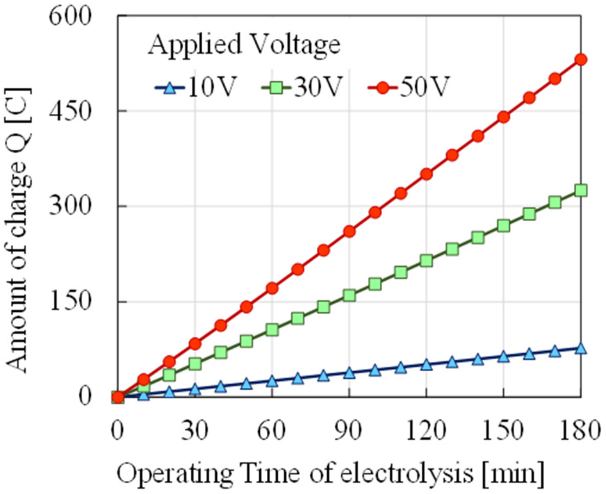


Fig. 6. Amount of charges as a function of the operating time between electrolysis.

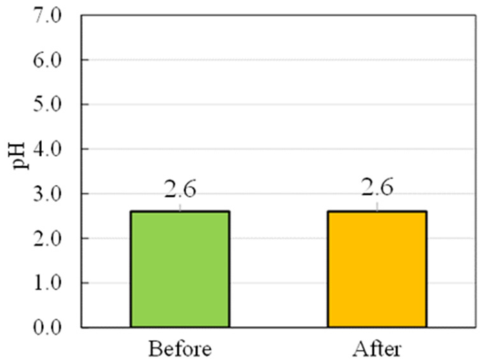
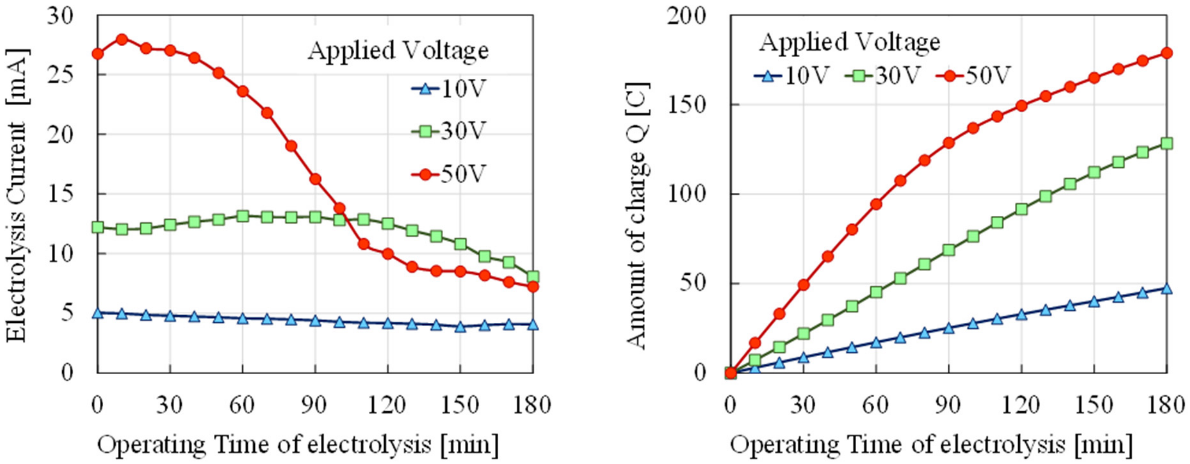


Fig. 7. pH of the solution before and after electrolysis.

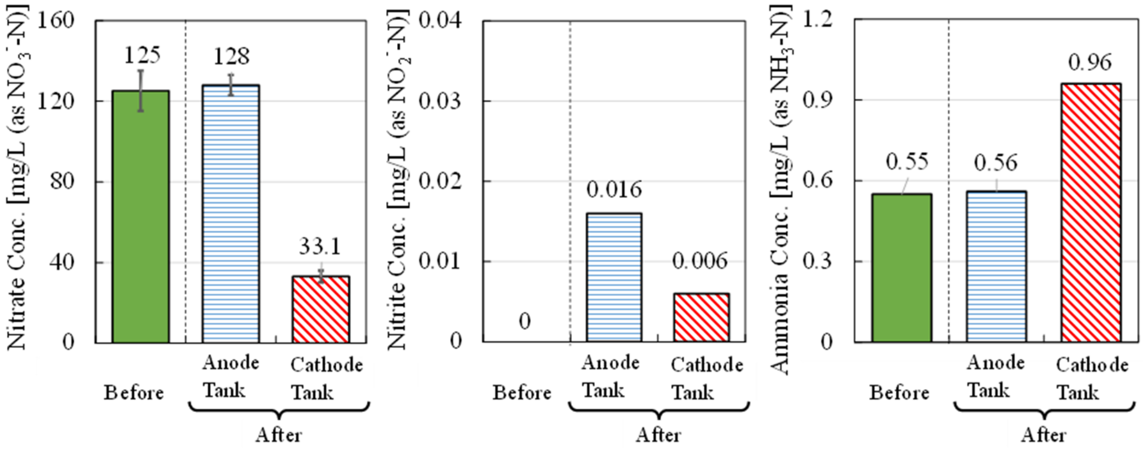
3.3 Effect of the dialysis membrane

Tests were conducted using the experimental apparatus described in Section 3.2 along with a means to separate the pretreatment solution in the electrolytic cell into an anode side and a cathode side by using a dialysis membrane. The time dependencies of the electrolysis current and the amount of charge during the electrolysis are shown in Fig. 8. The electrolysis current decreases with increasing operation time at an applied voltage of 50 V.



(a) Electrolysis current (b) Ammount of charge

Fig. 8. Electrolysis current and charge as a function of the electrolysis operating time for applied voltages of 10, 30, and 50 V.



(a) Nitrate concentration (b) Nitrite concentration (c) Ammonia concentration

Fig. 9. Changes in nitrate, nitrite, and ammonia concentrations in the anode and cathode tanks.

The differences in nitrate, nitrite, and ammonia concentrations before/after electrolysis at 50 V are shown in Fig. 9. In the cathode tank, the nitrate concentration decreased, and ammonia concentration increased as electrolysis proceeded and when the dialysis membrane was used. When the solution was electrolyzed, nitrite was generated at the cathode electrode, and it flowed into anode tank. Naturally, it is considered that the nitrite underwent oxidation to nitrate. The pH of the treatment solution after 3 h as a function of the applied voltage is shown in Fig. 10. In the cathode tank, the pH of the solution increases because of the decreasing nitrate concentration and increasing ammonium ion concentration. On the other hand, in the anode tank, the pH decreased slightly with increasing applied voltage.

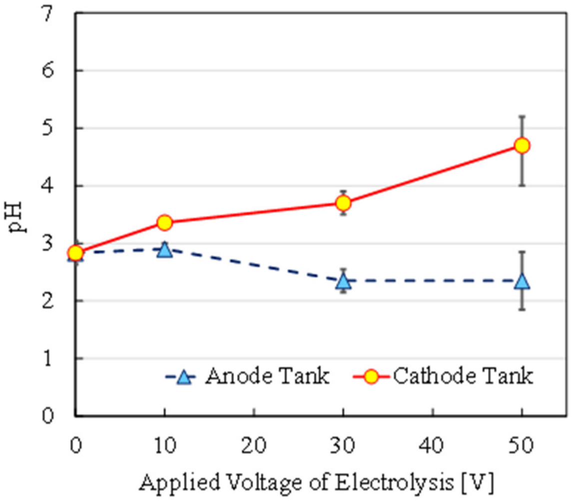


Fig. 10. pH of the solutions in the anode and cathode tanks as a function of the applied electrolysis voltage.

3.4 Effect of electrode area

In addition to the condition described in Section 3.2, a wide cathode electrode was used. Use of this cathode led to an increase in the cathode width from 10 mm to 30 mm. Therefore, the effective electrode area increased from 548 mm^2 to 1424 mm^2. The charge generated during electrolysis as a function of operating time is shown in Fig. 11. The effective electrode area increased 2.7 times compared to the conventional cathode; nevertheless, the charge increased slightly. The effects of the area of the cathode on the nitrate, nitrite, and ammonia concentrations are shown in Fig. 12. The nitrate concentration decreased, and the ammonia concentration increased, thereby increasing the pH. After electrolysis for 3 h, the pH of the solution was as shown in Fig. 13. The pH increased and reached 5.7 when using the wide cathode electrode.

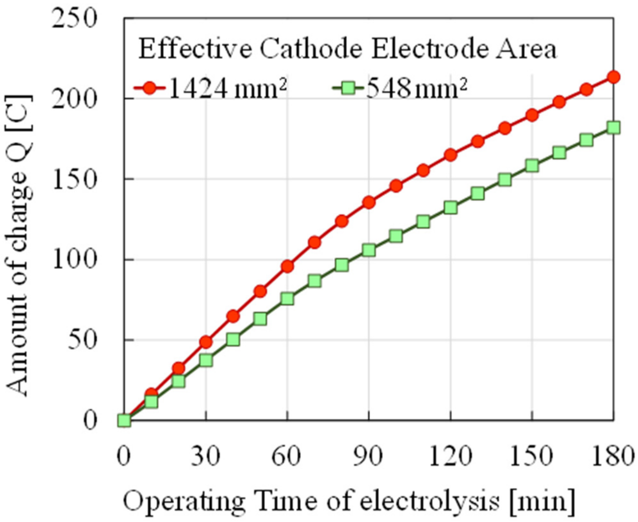
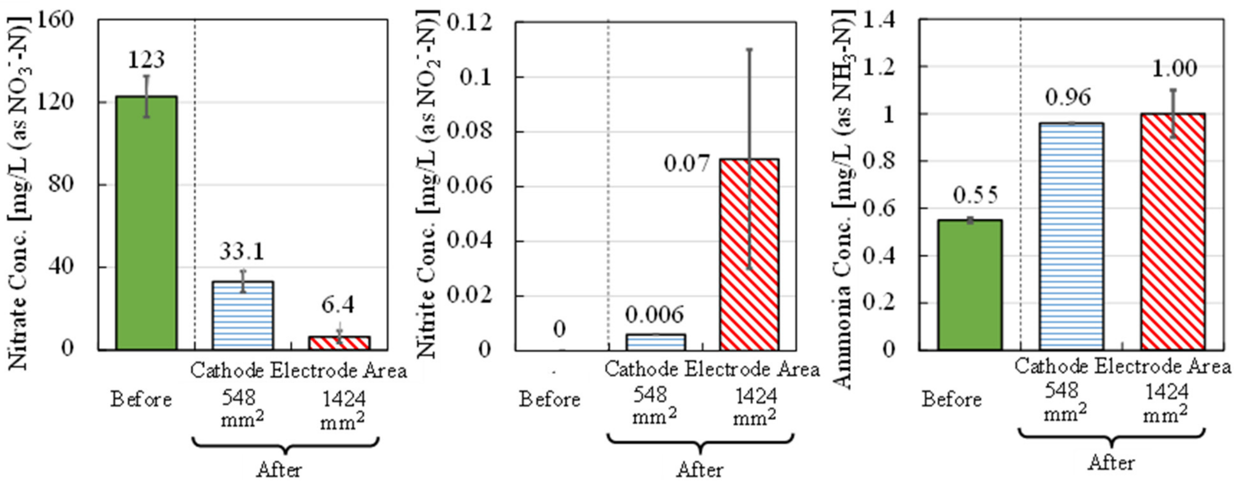


Fig. 11. Amount of charge as a function of operating time of electrolysis for different areas of the cathode electrode.



(a) Nitrate concentration (b) Nitrite concentration (c) Ammonia concentration

Fig. 12. Changes in the nitrate, nitrite, and ammonia concentrations with the cathode electrode area.

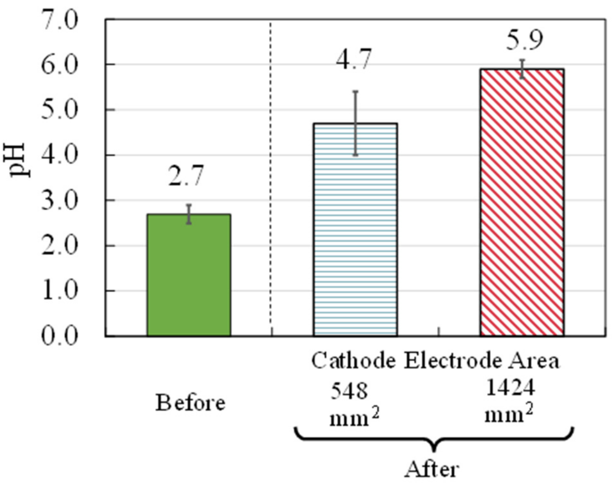


Fig. 13. Changes of pH of the solution for before and after treatment in the cathode tank.

3.3 Effect of stirring

In addition to the conditions described in Section 3.3 and 3.4, a stirrer bar set under the cathode electrode. Expected effects of the stirring is that the reaction source substance put closer to the electrode and the reaction products keep away from the electrode quickly. The amount of charge for electrolysis as a function of operating time is shown in Fig. 14. The area of wide cathode electrode was 1020 mm^2 after placing the stir bar under the cathode electrode. The amount of charge with stirring on the electrolysis as a function of operating time is shown in Fig. 14. The area of cathode electrode decreased to 1020 mm^2 from 1424 mm^2; however, the amount of charge increased with stirring. Furthermore, the charge did not decrease considerably compared to that when the area of the cathode electrode was 380 mm^2. The nitrate, nitrite, and ammonia concentrations are shown in Fig. 15. Nitrate and ammonia concentrations are higher compared to those without stirring. With stirring, nitrate flowed into the cathode tank from the anode tank through the dialysis membrane due to the influence of the concentration gradient. Therefore, the nitrate concentration increased. The pH characteristics are shown in Fig. 16. With stirring and using the wide cathode electrode, the pH of the solution after 3 h of electrolysis reached 6.8. The generation efficiency of the ammonia was 4.68 $\mu g\ C^{-1}$ without stirring, 7.48 $\mu g\ C^{-1}$ with stirring and an effective electrode area of 380 mm^2, and 10.5 $\mu g\ C^{-1}$ with stirring and an effective electrode area of 1020 mm^2. Hence, the generation efficiency of ammonia increased with stirring and the use of the wide cathode electrode.

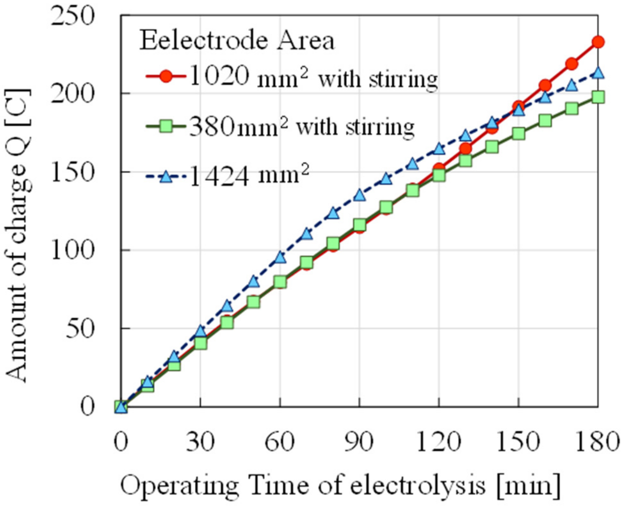
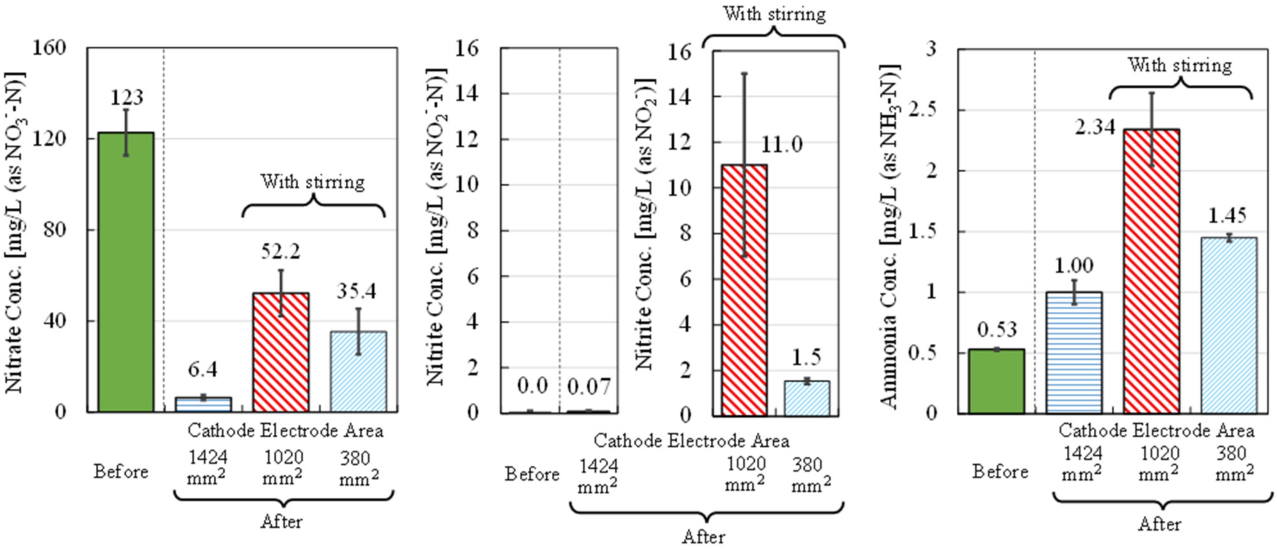


Fig. 14. Amount of charge as a function of operating time for electrolysis with stirring in the cathode tank.



(a) Nitrate concentration (b) Nitrite concentration (c) Ammonia concentration

Fig. 15. Changes in the nitrate, nitrite, and ammonia concentrations with stirring in the cathode tank

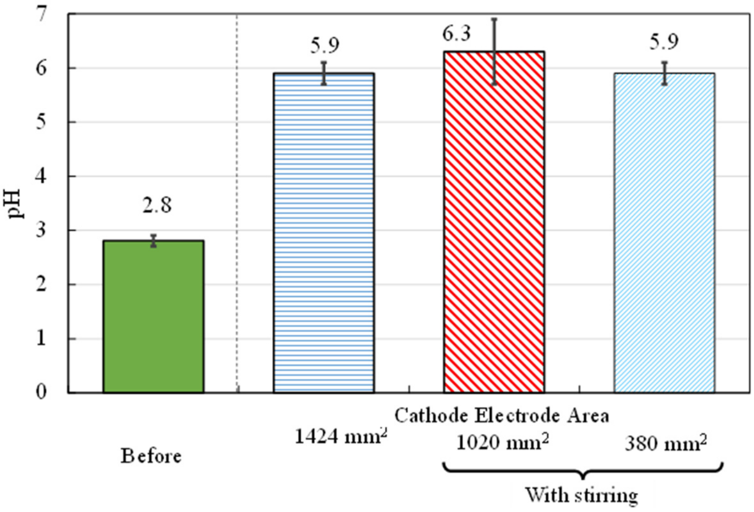


Fig. 16. Change of pH of the solution for electrolysis with stirring.

4. Conclusion

To generate nitrate and ammonia from the room air, a combination of the dielectric barrier discharge and electrolysis was tested. The pH of the solution decreased when the solution was bubbled with the air exposed by the dielectric barrier discharge. The aim of this study was to increase the pH of this solution with electrolysis. The results are as follows:

1. With only electrolysis, the current increased when the voltage increased; however, the pH did not increase.
2. When the electrolysis cell was separated with the dialysis membrane, the nitrate concentration in the cathode tank decreased, and the ammonia concentration increased with electrolysis. Hence, the pH of the cathode tank increased up to 4.8.
3. When the area of the cathode electrode increased, the amount of charge increased; in the solution of the cathode tank, the nitrate concentration decreased, and the ammonia concentration increased, and then the pH increased.
4. With electrolysis with stirring, the amount of charge increased even if the area of the cathode electrode was reduced, and then, the nitrate and ammonia concentrations also increased with stirring. The pH was the highest. This is the most effective technique—i.e., electrolysis with stirring.

From the above, a solution with a pH of 5.5 or higher could be obtained, and electrolysis could be performed according to the purpose. In the future works, ozone and any products from electrical discharge in the solution can be treated with electrolysis to obtain useful products.

References

[1] Chang, J.S., Kelly, A. J., and Crowley J. M., Handbook of Electrostatic Processes, Marcel Dekker, Inc., 1995.

[2] Cimerman, R., and Hensel, K., Generation of honeycomb discharge assisted by micro-hollow surface dielectric barrier discharge, *Int. J. Plasma Environ. Sci. Technol.*, Vol.15 (1), pp. e01003, 2021.

[3] Takaki K., Takahata J., Watanabe S., Satta N., Yamada O., Fujio T., and Sasaki Y., Improvements in plant growth rate using underwater discharge, *J. Phys.: Conf. Series*, Vol. 418, pp. 012140, 2013.

[4] Takano K., Takahata J., Takaki K., Satta N., Takahashi K., and Fujio T., Improvement of growth rate of *Brassica rapa var. perviridis* by discharge inside bubble under water in hydroponic cultivation, *IEEJ Trans. Fundam. Mater.*, Vol. 135 (8), pp. 467−472, 2015. (in Japanese)

[5] Ehara Y., and Takada A., Growth promoting effect for agricultural products by discharge products, *IEEJ Trans. Fundam. Mater.,* Vol. 135 (4), pp. 211−216, 2015. (in Japanese)

[6] Kawada Y., and Shimizu H., Generation of nitrogen compounds using barrier discharge and electrolysis, *J. Institute of Electrostatics Japan*, Vol. 41 (1), pp. 20−25, 2017. (in Japanese)

[7] Hiro N., Koizumi T., Rakuma T., Takaoka D., and Takizawa K., High-speed removal of nitrate from aqueous solutions by the electrolytic method, *Electrochemistry*, Vol. 70 (2), pp. 111−116, 2002. (in Japanese)

[8] Matsuo H., Sasao A., Nagafuchi Y., Ishibashi Y., and Nishikawa M., Experimental basis for purifying nitrate contaminated groundwater by electrolytic cell, *Annual Report of the Fukuoka Institute of Health and Environmental Sciences*, Vol. 30, pp. 131−136, 2002. (in Japanese)

[9] Comninellis, C., and Chen G., Electrochemistry for the Environment, Springer, 2010.

[10] Hong, J, Prawer, S., and Murphy, A.B., Production of ammonia by heterogeneous catalysis in a packed-bed dielectric barrier discharge: influence of argon addition and voltage, *IEEE Trans. Plasma Sci.*, Vol. 42 (10), pp. 2338−2339, 2014.

[11] Thagard, S. M., Kinoshita Y., Ikeda H., Takashima K., Katsura S., and Mizuno A., NO_3^- reduction for NOx removal using wet-type plasma reactor, *IEEE Trans. Ind. Applicat.*, Vol. 46 (6), pp. 2165−2171, 2010.