Air plasma electrolysis method for synthesis of liquid nitrate fertilizer with K_2HPO_4 and K_2SO_4 electrolytes

Harianingsih, Syarfina Farisah, Eva Karamah, Nelson Saksono*

Department of Chemical Engineering, Universitas Indonesia, Kampus Baru UI. Depok 16242,
Indonesia

* Corresponding author: nelson@che.ui.ac.id (Nelson Saksono)

Abstract

Nitrogen is a nutrient needed in a great amount to help plants grow and develop. Nitrogen is abundant in the atmosphere, typically around 78%; however, it is inert and cannot be directly absorbed by plants. Thus, fertilization is important to increase the nutrients available for plants. Air plasma electrolysis is an environmentally friendly technology that can initiate various reactions, including nitrogen fixation from the air into liquid nitrate fertilizer, with the production of reactive species, such as •OH and •H radicals. The main raw material is air, a freely available input. This research aimed to determine the production of liquid nitrate fertilizer through the air plasma electrolysis method by assessing the effect of electrolyte solution compositions and the air injection rate. This method was carried out in a batch reactor using a combination of K_2HPO_4 and K_2SO_4 as the electrolytes with concentration variations of 0.01 M and 0.02 M, airflow rate variations of 0.1–0.9 L min^{-1}, and a constant power of 700 W. The results showed that the greater the electrolyte concentration, the higher the conductivity of the solution, which facilitates electron generation as well as reactive species formed by electrolysis plasma to flow in the solution. The greater acidity value of the electrolyte solution (used at pH from 4 to 3.74) increased the number of electrons generated during electrolysis. The research demonstrated that a significantly increased nitrate production of 2213.5 mg L^{-1} (53.54 mmol) can be achieved at 0.8 L min^{-1} of air injection rate using a combination of 0.01 M K_2HPO_4 and 0.01 M K_2SO_4 electrolyte solutions.

Keywords: Air injection, fertilizer, nitrate, plasma electrolysis.

1. Introduction

Nitrogen is a nutrient needed by plants in a great amount to help them grow and develop properly, especially during the vegetative phase. Nitrogen plays a role as the basic component in proteins, amino acids, and enzyme synthesis, and also as an integral part of chlorophyll, which also controls the overall metabolic reactions that take place in plants [1]. Nitrogen is abundant in the atmosphere, as much as 78 % are in the form of N_2. However, nitrogen in the atmosphere is inert and cannot be absorbed by plants directly. Plants can easily absorb nitrogen if it is in the form of nitrate (NO_3^-) and ammonium (NH_4^+) ions [2]. Potassium and phosphorus play an important role in determining plant yield. When these elements are sufficient, there is an increase in enzyme activity, which also affects the increase in metabolic processes in plants.

The conventional Haber-Bosch process produces nitrogen fertilizers in the form of ammonia compounds by binding between nitrogen and hydrogen at high temperatures and pressures [3]. This process consumes 1–2 % of total energy production in the world and uses 2–3 % of the total natural gas produced, producing pollutants in the form of carbon dioxide of about 300 million tones in weight. However, ammonia production is a sustainable process emitting no greenhouse gases. Plasma technology is an environmentally friendly technology that can be the solution to fertilizer scarcity because it can produce liquid fertilizer that is rich in nitrates without producing residue and consumes 2.5 times lower energy than the Haber-Bosch process [4]. The raw material for the process is also available in abundance, as it only uses air as the main raw material. The energy for the process can be supplied using solar cells, which are also environmentally friendly technologies. However, there are still obstacles encountered in plasma technology when dissolving nitrite or

nitrate products into the liquid phase. The air plasma electrolysis process produces plasma in the liquid phase of water, where the air is simultaneously injected into the plasma [5, 6]. This method is effective in producing nitrate and is much better than plasma technology because nitrate is produced directly in the liquid phase. The injected air will react with reactive species from plasma to form nitrate compounds [7].

The electrolytes used in plasma electrolysis are K_2HPO_4 and K_2SO_4 to obtain better fertilizers. Potassium can be absorbed by plants in the form of K^+ and plays an important role in biochemical and biophysical processes in plants. Nitrogen plays an important role in plant vegetative growth and can be absorbed by plants in the form of nitrates (NO_3^-). The element phosphorus plays an important role in most enzyme reactions, which are phosphorylase dependent. Sulphur is a component of coenzyme A, biotin, and thiamine, which are very important hormones in carbohydrate metabolism. Plants can absorb the element S in the form of sulphates (SO_4^{2-}) [8]. The amount required for nitrogen needed by plants in general ranges from 100–250 mg L^{-1} [9]. This study examined how to make liquid nitrate fertilizer using the air plasma electrolysis method effectively and efficiently through optimum parameters such as the composition of the electrolyte solution and the airflow injection rate. Furthermore, the resulting nitrate product and nitrogen conversion can be seen.

2. Methods

The electrolyte solutions used were 0.01 M K_2SO_4, a mixture of 0.01 M K_2HPO_4 and 0.01 M K_2SO_4, a mixture of 0.01 M K_2HPO_4 and 0.02 M K_2SO_4, and a mixture of 0.02 M K_2HPO_4 and 0.01M K_2SO_4. The plasma electrolysis reactor was made of a quartz glass tube that has an inner diameter of 14 cm, with a cover at the top of the reactor. The reactor was equipped with two electrodes: a cathode and anode, a thermometer, and cooling water to control the temperature of the solution (Fig. 1). The cathode was in the form of a solid cylinder made of SS-316 stainless steel with a diameter of 6 mm. The anode was made of tungsten and was equipped with a special circuit for injection of air from the compressor, which was then channeled into the electrolyte.

The voltage at each electrolyte concentration was adjusted to obtain a constant electric power of 700 W. Nitrate concentration was measured with a UV-Visible spectrophotometry at a range of 0.01 mg to 1.0 mg NO_3^- N L^{-1} with a cuvette thickness (path length) 1 cm or more, at wavelength of 543 nm.
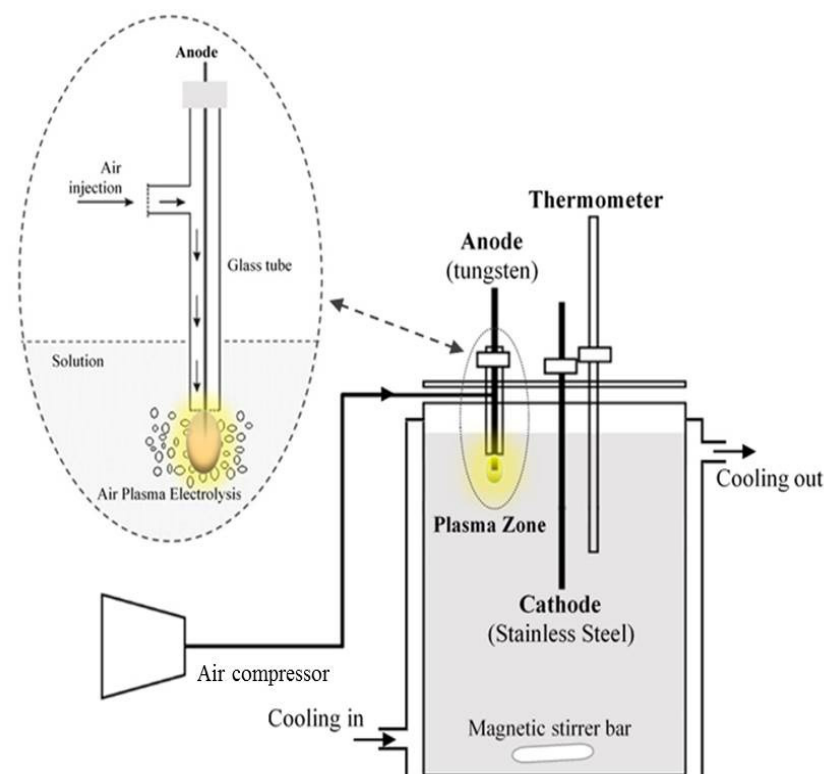

Fig. 1. Air plasma electrolysis reactor.

3. Results and discussion

3.1 Effect of electrolyte concentrations on nitrate production

Table 1 shows the increase in voltage with decreasing conductivity of the solution. This was due to the high conductivity of the solution increasing the electric current. If the power is kept constant, the voltage will decrease with increasing conductivity of the solution. The increase in operating voltage led to additional nitrate production.
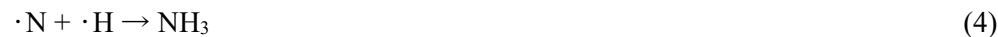
Table 1. Effect of electrolyte composition on conductivity, voltage, and nitrate production at 0.8 L/min air injection rate.

Electrolyte	Conductivity ($mS\ cm^{-1}$)	Voltage (V)	Nitrate production at 30 min	
			mmol	$Mg\ L^{-1}$
0.01 M K_2HPO_4 and 0.01 M K_2SO_4	2.40	547	53.54	2213.5
0.02 M K_2HPO_4 and 0.01 M K_2SO_4	3.37	522	43.17	1784.5
0.01 M K_2HPO_4 and 0.02 M K_2SO_4	3.48	510	40.25	1664.0
0.02 M K_2SO_4	4.72	403	36.99	1529.0

Table 1 shows that the highest nitrate production was obtained with an electrolyte solution combination of 0.01 M K_2HPO_4 and 0.01 M K_2SO_4, which yielded 2213.50 mg L^{-1} at a voltage of 547 V. Electrolyte solutions with a lower conductivity value produced higher nitrate because of the higher voltage used. A higher voltage influences the number and type of reactive species produced. At low voltages, •OH and •H radicals are generated, whereas at high voltages (above 490 volts), •O radicals appear in significant numbers [10]. The reaction between H_2O and O_2 with high-energy electrons (e*) in the plasma zone produces $\cdot$OH, •H, and •O radicals as in the reaction according to the following equations (1) and (2) [11].

$$H_2O_{(g)} + e^* \rightarrow \cdot H + \cdot OH + e^- \tag{1}$$

$$O_{2\ (g)} + e^* \rightarrow \cdot O + \cdot O + e^- \tag{2}$$

The •H radical species also encourages the nitrogen reaction from the air to become NH_3, while the presence of the •O radical species helps the process of nitrate formation in the presence of the nitrogen conversion to NO from the air, following equations (3), (4) and (5) [12,13].

$$N_{2(g)} + e^* \rightarrow \cdot N + \cdot N + e^- \tag{3}$$

$$\cdot N + \cdot H \rightarrow NH_3 \tag{4}$$

$$\cdot N + \cdot O \rightarrow NO \tag{5}$$

NH_3 and NO formed will be converted into nitrate through oxidation by •OH, O_2, and H_2O_2 [14]. Efforts to increase the effectiveness of the nitrate formation process can be carried out in two ways, as illustrated in Fig. 2. In the first pathway, N reacts with •O to form NO. This pathway can be achieved by increasing the formation of dissolved •O reactive species. A higher voltage can significantly increase •O formation. Therefore, it is necessary to assess the effect of a higher voltage on the formation of •O and nitrate products. Secondly, the •N reacts with •H to form NH_3, In this scheme, the effectiveness of the process is achieved by increasing the amount of •H and •OH production; however, the conversion of N_2 to •N is the rate-limiting step [12] in forming nitrate. This second pathway also needs •OH, H_2O_2, O_2 and HO_2^- [14], and the amount of •OH required is much greater. The use of higher voltages causes electrons to be excited in a stable gas envelope, forming plasma [15]. The contact of plasma with the solution can break down H_2O into hydroxyl (•OH) and hydrogen (•H) radicals. The plasma formed at the anode produces more •OH, whereas the plasma formed at the cathode

produces more $\cdot$H. For this reason, determining the effects of voltage, power, and plasma position (anodic and cathodic plasma) is necessary to assess the formation of hydroxyl (•OH), hydrogen (•H) and oxygen (•O) radicals, as well as the formation of nitrate products. The initial formation of the plasma is the conversion of N_2 and O_2 in the air by the plasma to N and O, while the H_2O vapor in the plasma zone will be converted to •H and •OH [6]

The reduction reaction of nitrate to nitrite can disrupt the equilibrium of the reaction of nitrate formation because the nitrate formed has been exposed to UV from plasma [14]. The pH condition of the solution, which decreases over time, also has an effect, as more acidic nitrate ions are formed when dissolved in water according to the following reaction [16].

$$3NO_{2\ (g)} + H_2O_{\ (l)} \leftrightarrow 2H^+ + 2NO_3^- + NO \tag{6}$$

Based on reaction (6), if the condition of the solution becomes more acidic, the absorption power of NO_2 gas, which is formed in the solution to become NO_3, will decrease, so that over time, the production of nitrate in the solution will decrease [15]. In subsequent experiments, the pH dropped from 4 at 30th minute to 3.79 at the 60th minute. According to Le Chatelier, low pH is a source of voltage for the system; however, the system needs to adjust its pH so it does not decrease. The time used for this process should not be too long due to the conversion, which is decreasing. The system will move the equilibrium between nitrate and nitrite towards the reactants, where the nitrate concentration decreases as it is converted back to nitrite. It is suspected that the resulting nitrate has been exposed to a significant amount of UV from the plasma, so that it has an impact on the equilibrium of the reaction of nitrate formation, which will initiate the reduction of nitrate to nitrite [14]. Therefore, a low pH will result in an equilibrium system towards nitrite and reduce nitrate concentration. High voltage affects the production of radicals during the plasma electrolysis process, where the increased production of radical varieties occurs with increased voltage [11]. Nitrate production increases with an increase in the number of •OH radicals [17]. High voltage also increases •O radicals. An increase amount of •O radicals has a positive impact on nitrate production, given that the formation of nitrates helps •O radicals to occur more concisely, compared to •H and •OH radical assistance.
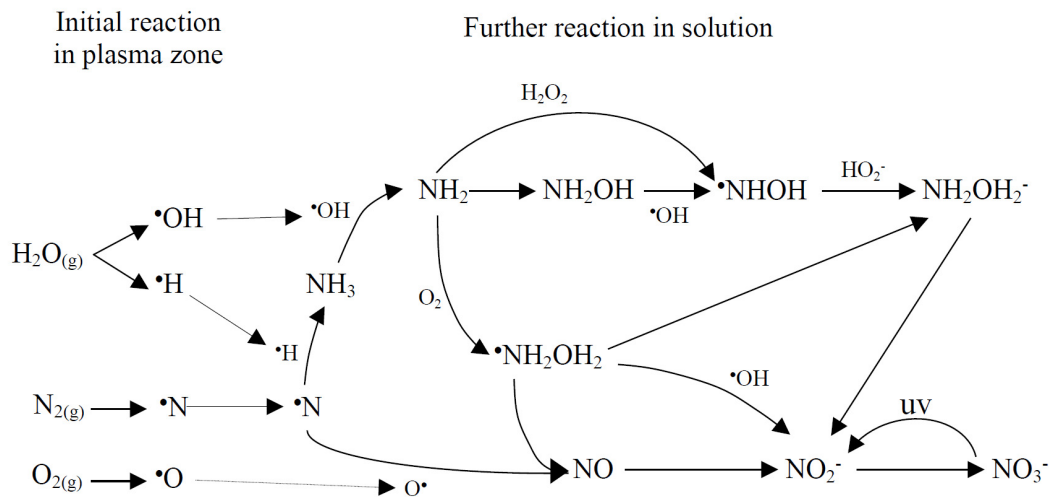

Fig. 2. Potential nitrate formation mechanism by air plasma electrolysis [6].

3.2 Effect of air injection rate

The optimum air injection rate point is the turning point obtained before any further increase in rate has an inefficient effect. Process conditions that are no longer efficient are indicated by the increase of the air injection rate that resulted in decreased nitrate production. The air injection rate represents the amount of raw material available to react with reactive species in the reaction for the formation of nitrates. If the air injection rate used is too large, it will result in the instability of the formed plasma, which will consequently affect the plasma performance in producing reactive species and eventually affect the formation of nitrates.
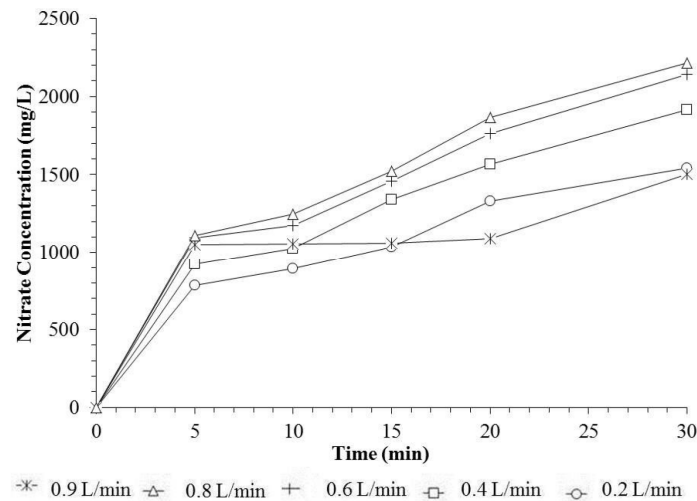
Fig. 3. Effect of air injection rate of 0.01 M K_2HPO_4 and 0.01 M K_2SO_4 on nitrate production.

As observed in Fig. 3, various air injection rates were carried out to determine the optimal air injection rate required in the nitrate synthesis process. With the increase in the air injection rate from 0.2 L min^{-1} to 0.8 L min^{-1}, there was an increase in nitrate production. The air injection rate of 0.8 L min^{-1} gave the best performance in producing nitrate at a concentration of 2213.5 mg L^{-1} at 700W. Visually, the plasma formed at each airflow rate looked different. At the air flow rate of 0.8 L min^{-1}, the plasma formed was greater than at the other flow rates. At 0.9 L min^{-1}, during the 5th to the 20th minute of the process, the increase in nitrate production was less significant, with an increase at the 30th minute, although the yield was still lower than at the flow rate of 0.2 L min^{-1}. The size of the plasma was large enough to almost touch the surface of the solution, such that the air turbulence around the anode became large and the stability of the plasma was disturbed. The more acidic the solution, the greater the NO_2 gas absorbed, which decreases the production of nitrate in the solution over time. N_2 and O_2 gases from the air will react more with the reactive species, especially •OH, to form nitrates. The species •OH is the reactive species with the highest level of oxidation to oxidize nitrogen from air to nitrate. Based on reaction (1), water molecules are split into •OH and •H due to the high energy electrons (e*) that are excited to the plasma. •OH radicals have a very short residence time of about 3.7×10^{-9} seconds [18] and can recombine with each other to form H_2O_2. O_2 gas can react with H_2O molecules to form H_2O_2 and O_3. Formation of the compound H_2O_2 will presumably increase the reaction of nitrogen or other intermediate NO_x compounds to form nitrate [19].

Table 2. Effect of air injection rate on amount of nitrate formed with 0.01 M K_2HPO_4 and 0.01 M K_2SO_4 solutions.

| Time (min) | 0.2 L min^{-1} (Air injection rate) | | 0.4 L min^{-1} (Air injection rate) | | 0.6 L min^{-1} (Air injection rate) | | 0.8 L min^{-1} (Air injection rate) | | 0.9 L min^{-1} (Air injection rate) | |
	NO_3^- (mmol)	N_2 conv* (%)	NO_3^- (mmol)	N_2 conv (%)	NO_3^- (mmol)	N_2 conv (%)	NO_3^- (mmol)	N_2 conv (%)	NO_3^- (mmol)	N_2 conv (%)
5	19.01	87.08	22.28	75.59	26.49	59.91	26.83	45.51	25.44	38.35
10	21.58	73.21	24.84	42.14	28.43	32.16	30.21	25.63	25.58	19.29
15	25.08	56.74	32.43	36.67	35.24	26.57	36.87	20.85	25.67	12.90
20	32.20	54.62	37.92	32.16	42.59	24.08	45.15	19.15	26.37	9.94
30	37.34	42.23	46.31	26.19	51.80	19.53	53.54	15.14	36.39	9.15

* N_2 conv = Nitrogen conversion.

Table 2 shows that an increase in the air injection rate of 0.2 L min^{-1} up to 0.8 L min^{-1} increased nitrate production. The air injection rate of 0.8 L min^{-1} provided the best performance in producing nitrate of 2213.5 mg L^{-1}. An increase in the air injection rate to 0.9 L min^{-1} resulted in a decline in nitrate production. This is because at high air injection rates, a phenomenon of degassing occurs due to the strength of the air that is injected into the solution. Degassing involves the transient gaseous passage from a dissolved gas (air injection)

in a liquid (electrolyte solution) [20]. Air injection rates too high could drive NO and NO_2 gas molecules dissolved in the solution to the environment. NO and NO_2 gases are intermediate compounds that play an important role in the formation process of nitrate. Therefore, in this case, if the degassing phenomenon continues, there will be a continuous decrease in these gas intermediates NO and NO_2, resulting in a decrease in nitrate production. An air injection rate of 1 L min^{-1} was tested; however, the process power at 700W could not be constantly maintained due to impaired plasma stability. Nitrogen conversion is the ratio of mmol of nitrate product to mmol of nitrogen in the air which is injected into the system. Highest nitrogen conversion for all variations in the composition of the electrolyte solution obtained in the first 5 minutes, where this indicates that the formation of nitrates occurs intensively in the first 5 minutes compared to the others. The highest conversion was achieved when the air injection rate was low, although it was less effective due to the low amount of nitrate products produced when the air feedstock used for the system was freely available. An increase in air injection rate was carried out until the optimum point (0.8 L min^{-1}) was reached, after which the nitrate production decreased along with the decrease in nitrogen conversion. As nitrogen conversion decreased, the process of nitrate formation became longer, unlike the initial minutes of intensive formation, thus saturating the system. Nitrogen conversion decreases with time but nitrate production increases over time for all air injection rates because no matter how big the air is injected into the system will not be a problem if the nitrated product produced is high and low energy consumption. A decrease in specific energy consumption has a good effect because the process costs required for electrical energy needs will increase low. Specific energy consumption is the ratio between electrical energy required for nitrate production. Based on this research, the optimal conditions for synthesizing liquid nitrate fertilizer are using a mixed electrolyte between 0.01 M K_2SO_4 and 0.01 M K_2HPO_4 at 700 W, an airflow rate of 0.8 L min^{-1}, anode depth of 1.5 cm, and the reaction time is 5 minutes with an energy consumption of 7.83 kJ $mmol^{-1}$. If the energy consumption by air plasma electrolysis is compared to the existing Haber-Bosch process in the industry, the energy requirements for the Haber-Bosch process are still much lower, which varies between 0.58 MJ mol^{-1} to 0.81 MJ mol^{-1} depending on the material source [21].

4. Conclusion

In this study, it was proven that plasma electrolysis by air injection at the anode is a technology that can be used to produce liquid nitrate fertilizers. The highest nitrate production was obtained by using a combination solution of 0.01 M K_2HPO_4 and 0.01 M K_2SO_4 at 700W, anode depth of 1.5 cm, air injection rate of 0.8 L min^{-1}, volume of 1.5 L, and system temperature in the range of 60 °C for 30 minutes of processing time. The total nitrate obtained was 2213.5 mg L^{-1} or 53.54 mmol, a nitrogen conversion rate of 15.14%. The higher the air injection rate until the optimum, the higher the nitrate production.

Acknowledgment

References

[1] Risnawati, R., Pengaruh pemberian pupuk urea dan beberapa formula pupuk hayati Rhizobium terhadap pertumbuhan dan hasil kedelai (Glycine max (L.) Merril) di lahan masam ultisol," Universitas Islam Negeri Maulana Malik Ibrahim, 2010. (*in Indonesian*)
[2] Tando, E., Upaya efisiensi dan peningkatan ketersediaan nitrogen dalam tanah serta serapan nitrogen pada tanaman padi sawah (Oryza sativa L.), *Buana Sains*, Vol. 18 (2), pp. 171–180, 2019. (*in Indonesian*)
[3] Modak, J. M., Haber process for ammonia synthesis, *Resonance*, Vol. 7 (9), pp. 69–77, 2002.
[4] Tanabe, Y., and Nishibayashi, Y., Developing more sustainable processes for ammonia synthesis, *Coordination Chemistry Reviews*, Vol. 257 (17-18), pp. 2551–2564, 2013.
[5] Salsabila, P., Haryansyah, A., and Saksono, N., Comparing nitrate production through CGDE (contact glow

discharge electrolysis) using Na_2SO_4 solution and K_2SO_4 solution, in AIP Conference Proceedings, Vol. 2175 (1), pp. 020003, 2019.

[6] Ardiansah, Salsabila, P., and Saksono, N., Effect of potassium sulfate concentration on synthesis of nitrate aqueous from the air using contact glow discharge electrolysis method, in AIP Conference Proceedings, Vol. 2255 (1), pp. 020002, 2020.

[7] Ren, J., Yao, M., Yang, W., Li, Y., and Gao, J., Recent progress in the application of glow discharge electrolysis plasma, *Open Chemistry*, Vol. 12 (12), pp. 1213–1221, 2014.

[8] Subandi,S., Pengelolaan Hara Kalium untuk Ubikayu pada Lahan Kering Masam, *Buletin Palawija*, Vol. 9 (22), pp. 86–95, 2013. (*in Indonesian*)

[9] Caliskan, O. and Kurt, D., Flower yields of pot marigold (Calendula officinalis L.) plants as effected by flowering durations and number of harvests, *J. Medicinal Plants Studies*, Vol. 6 (6), pp. 159–161, 2018.

[10] Liu, Y., Sun, B., Wang, L., and Wang, D., Characteristics of light emission and radicals formed by contact glow discharge electrolysis of an aqueous solution, *Plasma Chem. Plasma Proc*., Vol. 32 (2), pp. 359–368, 2012.

[11] Yasuoka, K., and Sato, K., Development of repetitive pulsed plasmas in gas bubbles for water treatment, *Int. J. Plasma Environ. Sci. Technol*, Vol. 3 (1), pp. 22–27, 2009.

[12] Peng, P., Li,Y., Cheng, Y., Deng, S., Chen, P., and Ruan, R., Atmospheric pressure ammonia synthesis using non-thermal plasma assisted catalysis, *Plasma Chem. Plasma Process*, Vol. 36, pp. 1201–1210, 2016.

[13] Hawtof, R., Ghosh, S., Guarr, E., Xu, C., Sankaran, R. M., and Renner, J. N, Catalyst-free, highly selective synthesis of ammonia from nitrogen and water by a plasma electrolytic system. *Science Adv.*, 5 (1), eaat5778, 2019.

[14] Wang, J., Song, M., Chen, B., Wang, L., and Zhu, R., Effects of pH and H_2O_2 on ammonia, nitrite, and nitrate transformations during UV 254 nm irradiation: Implications to nitrogen removal and analysis, *Chemosphere*, Vol. 184, pp. 1003–1011, 2017.

[15] Thagard, S. M. Kinoshita, Y. Ikeda, H. Takashima, K. Katsura, S., and Mizuno, A., NO_3^- Reduction for NO removal using wet-type plasma reactor, *IEEE Trans. Ind. Applicat.*, Vol. 46 (6), pp. 2165–2171, 2010.

[16] Burlica, R. Kirkpatrick, M. J., and Locke, B. R., Formation of reactive species in gliding arc discharges with liquid water, *J. Electrostat.*, Vol. 64 (1), pp. 35–43, 2006.

[17] Wang, J., Yu, L., Hu, L. Chen, G. Xin, H. and Feng, X., Ambient ammonia synthesis via palladium-catalyzed electrohydrogenation of dinitrogen at low overpotential, *Nature Commun.*, Vol. 9 (1), pp. 1–7, 2018.

[18] Ruma, H. M., Hosseini, S., Sakugawa, T., and Akiyama, H., Treatment of wastewater by underwater discharge in gas bubbling water, *Int. J. Renewable Energy Environ. Eng.*, Vol. 3 (3), pp. 189–194, 2015

[19] Jiang, B., Zheng, J., Qiu, S., Wu, M., Zhang Q., Yan, Z., and Zue, Q., Review on electrical discharge plasma technology for wastewater remediation, *Chemical Eng. J.*, Vol. 236, pp. 348–368, 2014.

[20] Saksono, N., Febiyanti, I. A., Utami, N., and Ibrahim, "Hydroxyl radical production in plasma electrolysis with KOH electrolyte solution," in AIP Conference Proceedings, Vol. 1699 (1), pp. 060013, 2015.

[21] Hollevoet, L., Ras, M.D., Roeffaers, M., Hofkens, J., and Martens, J.A., Energy-efficient ammonia production from air and water using electrocatalysts with limited faradaic efficiency. *ACS Energy Lett.*, Vol. 5 (4), pp.1124–1127, 2020.