

The Effect of Power on Nitrate Synthesis and The Emission Intensities of Reactive Species Using Anodic Plasma Electrolysis

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Abstract. Nitrates are used as fertilizer to fulfill nutrients for plants. Anodic plasma electrolysis technology can be an effective and environmentally friendly solution in nitrogen fixation into nitrate compounds. This research aimed to determine the effect of controlling voltage and power in nitrate synthesis using plasma electrolysis with air as the raw material injected at the anode. The material used is an electrolyte solution of 0.02 M K₂SO₄, the electrodes used are in the form of tungsten and stainless steel, and a nitrate reagent is used for the nitrate test. The results of the study showed that at 400 W, the optimal rate was 0.8 L men⁻¹ with 1889 mg L⁻¹ of nitrate formed. While at 500 W and 600 W, the optimal rate of 1 L men⁻¹ with nitrate formed was 2213 mg L⁻¹ and 2453 mg L⁻¹. The emission intensities of reactive species N, N₂^{*}, N₂⁺, •OH, •H, and •O at an optimal rate of 0.8 L men⁻¹ 400 W 700 V in 20139 au, 28540 au, 18023 au, 30863 au, 12547 au, 49800 au. The addition of air injection will increase the oxygen input into the plasma zone, which can produce reactive species •O and nitrogen produces reactive species N, N₂^{*}, N₂⁺ forms NO. The formed NO compounds can be oxidized to NO₂, and the reaction between NO₂ and reactive species •OH forms nitrates.

Keywords: Air Injection, Anodic Plasma Electrolysis, Emission Intensities, Nitrate, Reactive Species

INTRODUCTION

Nitrate synthesis through nitrogen fixation is carried out naturally with biological fixation in the form of a nitrification process. where ammonia compounds are converted

into nitrate compounds with the help of nitrifying bacteria, which then nitrate will be absorbed by plants (Ingels and Grave, 2015). Nitrates from the nitrification process that are absorbed by plants are not able to meet 100-250 ppm of nitrogen needs from plants

(Wang et al., 2017a). Industrial nitrogen fixation through the conventional Haber-Bosch process has been known to produce nitrogen fertilizers in the form of ammonia compounds by binding between nitrogen and hydrogen at high temperatures and pressures. Haber Bosch requires energy for the steam reforming process when taking hydrogen gas from natural gas (CH₄). This process also produces high CO₂ emissions (Rouwenhorst et al., 2020). This process consumes 1-2% of total energy production worldwide and uses 2-3% of the total natural gas produced. This process also produces 300 million tons/year of pollutants in the form of carbon dioxide (Wang et al., 2018). Ammonia is a chemical compound that contributes to 75% of greenhouse gas emissions (Soloveichik et al., 2019). The unsatisfied need for nitrate for plants through natural nitrogen fixation or nitrogen fixation technology that is less environmentally friendly. Coupled with the increasing need for fertilizers, it has encouraged the existence of environmentally friendly nitrogen fertilizer synthesis technology. Air plasma technology can be used as an alternative because it can produce nitrate in an environmentally friendly process. The energy consumption of air plasma is also 2.5 times lower than the Haber-Bosch process (Wang et al., 2017b). The production of nitrate using plasma requires electricity, which can be supplied from fossil fuels or renewable energy. However, the nitrate needed by plants is easily absorbed in the liquid state. While the air plasma technology produces a low nitrate yield in the liquid phase. This is because the diffusion process of NO and NO₂ gases produced from air plasma into the liquid phase to form NO₃⁻ is still low. In addition, the reactive species of •OH and •H needed for nitrate formation are relatively small (Farwan

et al., 2021). Air plasma technology which produces a low nitrate yield in the liquid phase, encourages the use of the plasma electrolysis method. The synthesis of liquid nitrate by plasma electrolysis method uses air as the main raw material for the required nitrogen source (Li et al., 2018). The nitrate formation in this reaction is dominated by the role of •OH and the nature of •OH in oxidizing NH₄⁺ to NH₃ and then forming NO₃⁻ which takes place rapidly (Sakakura et al. 2020).

The final nitrogen product obtained is in the form of nitrate, while the ammonium formed will be rapidly oxidized to ammonia which will be further oxidized to nitrate. This phenomenon makes the amount of ammonium produced small. The initial formation of the plasma reaction is the conversion of air by plasma becomes •N and •O, while the H₂O vapor in the plasma zone will be converted into •H and •OH (Luvita et al. 2022). The increase in power is accompanied by an increase in stress, causing an increase in the number of •H and •OH on process performance. Plasma electrolysis is generally observed with increasing power (Tang et al., 2018). This research proves that increasing electric power at constant voltage will increase the number of reactive species produced (increasing reaction conversion).

As the demand for nitrate fertilizers increases, nitrogen fixation for nitrate synthesis using catalysts and existing biological methods uses high energy and emissions that cause environmental problems. This phenomenon triggers the emergence of nitrogen fixation using plasma technology that is environmentally friendly and supports energy savings. However, the nitrate produced is still low, and the product is in the form of a gas that is difficult to process further into fertilizer. Plasma electrolysis overcomes the drawbacks of

plasma technology due to its higher conversion of dissolved nitrate. While the increase in voltage at constant power changes the composition of reactive species produced (increasing the selectivity of the reaction). Next, We observe the process's effectiveness by measuring nitrate production and energy consumption at various power at a constant voltage. The process's effectiveness was also observed at various voltages at constant power. So the purpose of this study is to determine the effect of power and emission intensity on the formation of reactive species on nitrate production. In addition, it is also observed semi-quantitatively by reactive species $\bullet\text{N}$, $\bullet\text{N}_2^*$, $\bullet\text{N}_2^+$, $\bullet\text{OH}$, $\bullet\text{O}$, and $\bullet\text{H}$ are produced.

MATERIALS & METHODS

The materials used in this study include nitrogen (79%), oxygen (21%), MERCK potassium sulfate 1.05153.0500 with 99% purity dissolved in distilled water as electrolyte, HACH, Nitrate test reagent 2106169. Nitrite test using cadmium sulfate MERCK hydrate 1.02027.0100 (with specifications Chloride $\leq 0.001\%$, nitrogen $\leq 0.0005\%$, copper $\leq 0.0005\%$, Iron ≤ 0.0005 , Potassium $\leq 0.01\%$, Sodium $\leq 0.005\%$, Calcium $\leq 0.005\%$, Lead $\leq 0.002\%$ and Zinc $\leq 0.002\%$), Copper (II) MERCK sulfate pentahydrate 1,02790,1000 with 99% purity and N-(1-naphthyl)-ethylenediamine dihydrochloride (NED) MERCK 106237 with 99% purity.

The cylindrical reactor made of glass with a volume capacity of 1.2 liters is equipped with a temperature sensor, condenser, power analyzer, AS SUS 316 DIA 5 mm stainless steel electrodes, and tungsten EWTH-2 RHINO GROUND measuring 1.6 mm x 175 mm and powered by a power supply tension. DC

power supply voltage and current can be adjusted from 0 to 1000 Volts and 0 to 5 A, respectively. Tungsten as the anode is placed in a glass casing, and the length of the tungsten immersed in the electrolyte solution at the end of the casing is 5 mm. The series of research experimental tools used in the study equipped with temperature sensors are shown in Figure 1.

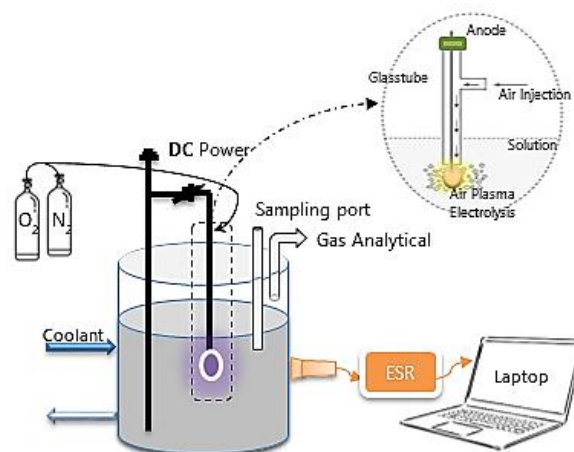


Fig. 1: Anodic Plasma Electrolysis Schematic

Several other tools used are test equipment, UV-VIS spectrophotometer (BEL Engineering UV-M51 Single beam spectrophotometer) for nitrate, nitrite, and ammonium tests. The nitrate level test was carried out using the UV-VIS Spectrophotometer method at a wavelength of 410 nm with a concentration range of 0.1 mgL^{-1} to 2.0 mgL^{-1} (SNI 06-2480-1991). Determination of nitrite was carried out with a UV-VIS spectrophotometer at a wavelength of 543 nm. The concentration range is 0.01 mgL^{-1} to 1.0 mgL^{-1} . Acidic atmosphere (pH = 2-2.5) (SNI 06-6989.9-2004). Ammonia determination was carried out by UV-VIS spectrophotometer at a wavelength of 640 nm with a concentration range of 0.1 mgL^{-1} to 0.6 mgL^{-1} $\text{NH}_3\text{-N}$ (SNI 06-6989.30-2005). Analysis of the emission spectrum intensity used Electron Spin Resonance (ESR) which was connected to an optical probe, carried out in a dark room to

determine the gas formed in the reactor due to the release of plasma at the electrode. The ESR for identification of the emission intensity of reactive species is equipped with an X-band bridge (9.2GHz), high-sensitivity resonator (Bruker ER 4119HS, Germany), 20 mW microwave power, 1 G modulation amplitude, 100 kHz modulation frequency, 14 G sweep width, sweep time 60sec, center field 336mT. All spectra were collected in atmospheric air, at 30.8°C, using a temperature controller and gas (NoxygenNOX-E.4-TGC, Germany) in the field ranging from 312 to 360 mT. Stable reactive species concentrations were assessed using microwave total absorption data evaluated by first-derived double integration of the ESR spectrum. ESR spectrum can be generated by varying the incident frequency photon on the sample by giving a constant magnetic field or do on the contrary (Sensi & Senesi, 2022). In practice, usually, the frequency is kept constant. Central group paramagnetic, such as free radicals, hit microwaves at a fixed frequency (S. Jiang et al., 2020). This eliminates other light waves received by the camera, as it is tuned at 200–1100 nm with a very high UV-NIR response sensitivity. Based on this study, using an ICCD (Intensive CCD) camera placed perpendicular to the plasma splash, where the signal time remained at 1 ms.

RESULTS AND DISCUSSION

Nitrate Production and Specific Energy on Different Powers

The condition for the formation of anodic plasma electrolysis is the formation of a gas envelope around the anode, which causes resistance to electron flow and triggers a discharge in the form of plasma. This gas envelope can be formed from the

evaporation of water around the anode due to the Joule heating effect (Farisah et al., 2021). The gas envelope can also be formed by the injection of gases, such as air, around the anode so that the evaporation energy of water can be suppressed in the anodic plasma formation process. Air injection in the plasma zone will reduce the electrical energy consumption of the plasma electrolysis process and trigger the formation of new reactive species such as $\bullet\text{N}$, $\bullet\text{N}_2^*$, and $\bullet\text{O}$. Air with the air injected into the electrolyte solution in the plasma electrolysis process is the raw material for the reaction of nitrate formation. N_2 and O_2 gases from the air will react more with reactive species, especially $\bullet\text{OH}$ and $\bullet\text{O}$, to form nitrate (Budikania et al., 2019). In addition, the injection of air at the anode helps reduce the effect of erosion or eroding of the anode, thereby increasing the effectiveness of the process. Table 1 shows that increasing the flow rate of air injection, in general, is able to increase the production of nitrate while reducing its specific energy consumption at various given electrical power.

Table 1 shows the optimum air flow rate at various power variations. At 400 W, the optimum flow rate was obtained at 0.8 L men^{-1} with a nitrate production of 36.56 mmol. The optimum flow rate and power of 500 W and 600 W occurred at 1 L men^{-1} with nitrate production of 42.84 mmol and 47.47 mmol. Nitrate production increases as the airflow rate increase up to 0.8 L men^{-1} . Higher than 0.8 L men^{-1} airflow rate, nitrate production decreased. This phenomenon indicates that air injection positively impacts nitrate formation due to the addition of bubbles and increases the stability of the gas envelope at the anode end where plasma is formed. Chen et al. (2021) find that the presence of gas bubbles and envelopes in the plasma zone

Table 1: Nitrate Production and Specific Energy at Different Powers

Power (W)	Air Injection Flowrate (L men ⁻¹)	Nitrate Production		Specific Energy (kJ mmol ⁻¹)
		mg L ⁻¹	mmol	
400	0.2	1027	19.87	72.46
	0.4	1340.5	25.94	55,51
	0.6	1567.5	30.33	47.47
	0.8	1889	36.56	39.39
	1	1534	29.69	48.51
500	0.2	1175,5	22.75	79.13
	0.4	1457	28.20	63.84
	0.6	1760,5	34.07	52.83
	0.8	2023	39.15	45.98
	1	2213	42.84	42.02
600	1.2	1963	37.99	47.38
	0.2	1249	24.17	89.37
	0.4	1524	29.49	73.24
	0.6	1866.5	36.12	59.80
	0.8	2141.5	41.44	52.12
	1	2453	47.47	45.5
	1.2	2196	42.5	50.83

will increase the average length of the free electron path and the excitation speed of the ionization of water molecules in solution and produce more reactive species both in the form of radicals or ions.

The decrease of nitrate production when the air flow rate exceeds the optimum value can occur due to degassing and plasma stability factors. Degassing phenomenon is the process of entering gas into a solution to move dissolved molecules in the solution to the gas phase. An airflow rate that is too strong will make the NO and NO₂ gas molecules dissolved in the solution pushed into the environment (Wang et al., 2017b). Turbulence in the gas envelope around the anode due to the high air injection flow rate destabilizes the plasma and reduces the

plasma's ability to produce reactive species, thereby decreasing nitrate formation. Stable plasma is formed if the gas envelope in the plasma zone is stable; the larger the plasma formed, the larger the gas envelope required. Basically, the injection of air in the plasma zone will facilitate the formation of a stable gas envelope, but if the air injection is too high, it will disrupt the stability of the gas envelope so that the plasma formed becomes unstable. An increase in electrical power will increase the plasma and gas envelope size, thus requiring a higher air injection rate. Therefore, if this phenomenon continues, it will have an impact on decreasing intermediate compounds such as NO and NO₂ gases and will have an effect on reducing nitrate yield. This phenomenon is caused by

the presence of air injection, which triggers the emergence of reactive species such as $\bullet\text{H}$, $\bullet\text{O}$, and $\bullet\text{OH}$ (Firawan et al., 2021). Air is used as raw material for nitrate synthesis, wherein in the free air, O_2 and N_2 components will react with reactive species to encourage nitrate production. One type of reactive species that plays an important role in nitrate production is $\bullet\text{OH}$. A lot of $\bullet\text{OH}$ is generated due to gas ionization due to the heating of joules in solution (Tsuchida et al. 2021).

The specific energy consumed at the same power decreases as the airflow rate increases as the nitrate produced increases to the optimal airflow rate. After reaching the optimum point, the specific energy consumed will increase again. This condition is inefficient and indicates an increase in air flow rate needs to be stopped. At 400 W, the lowest specific energy consumption is achieved at an airflow rate of 0.8 L men^{-1} and increases again at 1 L men^{-1} . While at 500 W and 600 W, the lowest specific energy consumed is achieved at 1 L men^{-1} air flow rate and increases again at 1.2 L men^{-1} . This phenomenon occurs because the production of nitrate rises along with the increase in air flow rate until it reaches the optimum air flow

rate, but after passing the optimum point, the amount of specific energy consumption will increase again, so that in that condition it is no longer efficient and the increase in air flow rate needs to be stopped. It also shows that there is an optimum flow rate condition at different power in the formation of nitrate. The lowest air flow rate shows the highest energy consumption curve due to the smallest nitrate production. Thus, it can be concluded that the amount of specific energy consumption is inversely proportional to the amount of nitrate produced. Power also affects the formation of plasma, so Figure 2 (a)(b)(c) can be seen plasma flame at different powers.

Figure 2 shows that the higher the power, the plasma flame will be bigger and brighter. This phenomenon is caused by the relationship between power and energy transferred to electrons. The high power indicates the energy transferred to the plasma is also getting bigger. The presence of high energy causes electrons to be easily excited, increasing the production of electrons leaving the orbit so that the radical compounds are higher and the plasma produced is brighter (Sen Gupta, 2017).

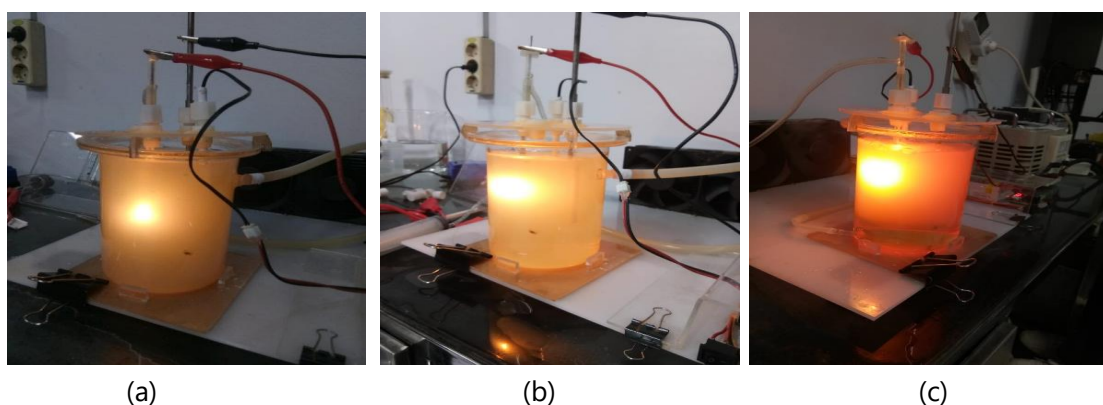


Fig. 2: Anodic Plasma Electrolysis Flame in different Powers (a) 400 W, (b) 500 W, (c) 600 W

Table 2: Emission Intensities of Reactive Species on 0.8 L men⁻¹, 400 W

Voltage (V)	Emission Intensities of Reactive Species * (au)						Nitrate (mg L ⁻¹)	Nitrite (mg L ⁻¹)	Ammonia (mg L ⁻¹)
	•N	•N ₂ *	•N ₂ ⁺	•OH	•H	•O			
500	12436	19823	13624	13625	10805	38259	1326	164.8	21.8
600	13625	21893	13321	24671	11001	45413	1401	200.7	23.6
700	20139	28540	18023	30863	12547	49800	1889	350.3	29.1

wavelength : •OH (306 nm), •H (654 nm), •O (844 nm), •N₂ (317 nm), •N₂⁺ (479 nm), •N (777 nm)

Emission Intensities of Reactive Species Generations

The voltage applied during the plasma electrolysis process plays an important role in the formation of reactive species and the amount of nitrate formed. The emission intensities of reactive species and nitrate products are shown in Table 2 and Figure 3. Table 2 shows the number of reactive species produced at various electrical voltages. The increase in voltage from 500 V to 700 V increased the reactive species •N, •N₂*, •N₂⁺, •OH, •H, •O and nitrate production by 60%, 44%, 32%, 127%, 16%, 30%, and 42% respectively. The same thing explains that increasing the voltage can increase the temperature of the electrons, thereby increasing the population of high-energy electrons (Girald et al., 2016). The emission intensity of reactive species does not form below 500 V, and the electron energy is not high enough to produce excited atoms. The simultaneous formation of nitrate was carried out at the same power, namely 400 W with a voltage of 500 V, 600 V, and 700 V, through strong current engineering. Low current strength produces a large electric voltage. During the process, the power is kept constant to obtain accurate data, and the process energy consumed during the plasma electrolysis process remains the same so that a comparison can be made between the nitrate concentration and the reactive species composition produced with different voltages. Then the greater the voltage, the

number of reactive species produced also increases for all types of reactive species. Increasing the voltage contributes to increasing radicals in the solution (Liu et al., 2012).

Figure 3 shows that high electron energy at high voltage makes the electron easily excited. Therefore, more electrons will be excited from its orbit. This phenomenon makes the plasma brighter and produces more radical species (Ito et al., 2016). Voltage affects the selectivity of the resulting species. Hydroxyl radicals begin to appear at 500 V. As the voltage increase to 700 V, the production of •N, •N₂*, •N₂⁺, •OH, •H, and •O also increases but is sufficient to increase the formation of nitrate and •OH radicals because they cause the formation of NO and NO₂. Nitrogen reactive species also influence nitrate formation via the NO pathway. This condition is caused by a high voltage which has an impact on the energy given to the electrons is also higher. Water molecules in the gas phase dissociate to form OH in the gas phase that diffuses into the solution. The electrons formed in the releasing plasma also react with water molecules at the gas-liquid interface to form •OH (Rumbach et al., 2013). In the reaction equation and the number of reactive species. It can be seen that the effective pathway for nitrate formation is through NO formation. As the voltage increase, the number of reactive species also increases, particularly •O and •OH species that reach 49800 au and 30863 au at 700 V.

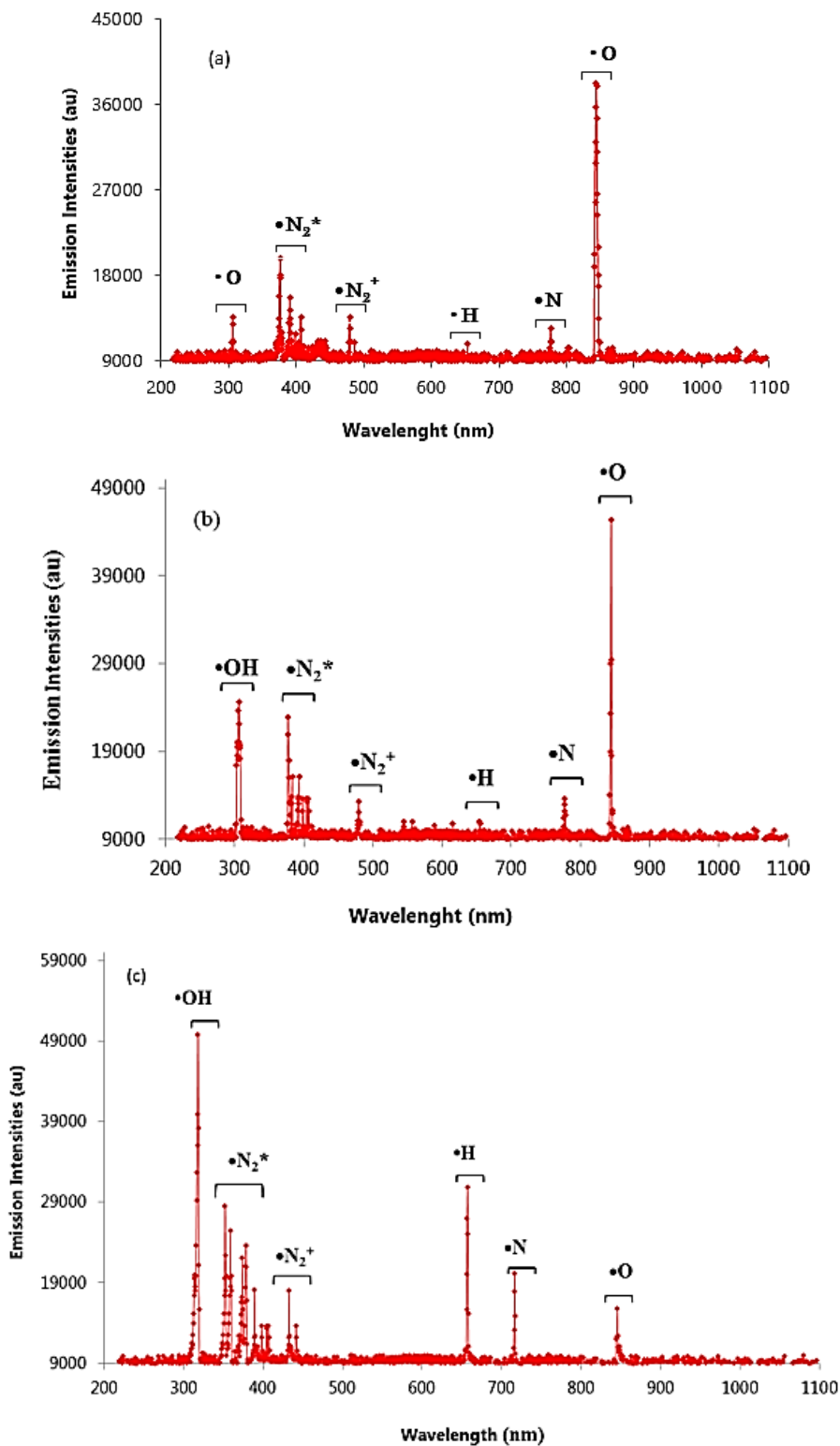


Fig. 3: Emission Intensities on 400 W, (a) 500 V, (b) 600 V, (c) 700 V

This phenomenon is in accordance with the research conducted by Liu et al. that there is an increase in $\bullet\text{O}$ under these conditions

when the same energy is applied to the input (400 W) at each voltage variable. This phenomenon also indicates a high oxidation

state of $\bullet\text{O}$ and $\bullet\text{OH}$, namely 2.4 eV and 2.7 eV. So, they are strong enough to form NO , which is oxidized by $\bullet\text{OH}$ to form NO_2 and then NO_3 (Wang et al., 2017a).

CONCLUSIONS

This study concludes that anodic plasma electrolysis can be used for nitrate synthesis. At 400 W, the lowest specific energy consumption is achieved at an airflow rate of 0.8 L men^{-1} . While at 500 W and 600 W, the lowest specific energy consumed is achieved at an airflow rate of 1 L men^{-1} . It also shows that there are conditions of effective flow rate at different power in the formation of nitrate. The increase in voltage increases the formation of $\bullet\text{O}$. At 700 V, the increase in $\bullet\text{O}$ formation is very significant.

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