Journal of Advanced Research in Fluid Mechanics and Thermal Sciences

Journal homepage:
https://semarakilmu.com.my/journals/index.php/fluid_mechanics_thermal_sciences/index
ISSN: 2289-7879

The Effect of Fe^{2+} Ions Addition on Reactive Oxygen and Nitrogen Species (RONSs) with Controlled Initial pH of Nitrate Synthesis using Plasma Electrolysis Reactor

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ARTICLE INFO

Article history:
Received 12 August 2024
Received in revised form 30 November 2024
Accepted 9 December 2024
Available online 20 December 2024

Keywords:
Fenton reaction; initial pH; nitrate production; plasma electrolysis; RONSs

ABSTRACT

Plasma electrolysis offers an environmentally friendly approach to nitrate synthesis. This study aimed to investigate the effect of Fe^{2+} ion addition on the formation of reactive oxygen and nitrogen species (RONSs) and nitrate production under controlled initial pH conditions (pH = 6). The experiment utilized a plasma electrolysis reactor with a 0.02 M K_2SO_4 electrolyte, an air flow rate of 0.8 L/min, Fe^{2+} ions at a concentration of 30 ppm, and a temperature of 60°C. Nitrate production was measured using a UV-VIS spectrophotometer, while RONSs emission intensity was analyzed using an electron spin resonance (ESR). The results showed that with and without the addition of Fe^{2+} ions accelerated the pH drop from 6 to 3 in just 60 minutes. Nitrate production increased significantly with Fe^{2+}, reaching 2432 ppm compared to 2046 ppm without Fe^{2+}. RONSs emissions without Fe^{2+} included •OH (306 nm), •H (654 nm), •O (844 nm), N_2 (317 nm), N_2^+ (416 nm), and N (777 nm). With Fe^{2+} addition, the emission intensities of these species remained consistent, indicating the role of Fe^{2+} in enhancing nitrate production without significantly altering RONSs profiles.

1. Introduction

Nitrate synthesis is the process of making nitrate compounds that are important in various applications, especially in the fertilizer industry to meet the nitrogen needs of plants. Nitrate is a form of nitrogen that can be directly absorbed by plant roots and plays a vital role in plant growth and development [1]. Naturally, nitrate synthesis occurs through the nitrification process in the nitrogen

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https://doi.org/10.37934/arfmts.125.2.170179

cycle. This process involves nitrifying bacteria that oxidize ammonia (NH_3) to nitrite (NO_2^-) and then to nitrate (NO_3^-). However, the amount of nitrate produced naturally is often insufficient for plant needs, especially on an intensive agricultural scale. In industry, nitrate synthesis is usually carried out through the Ostwald process [2]. This process involves the oxidation of ammonia to nitrogen monoxide (NO) using a catalyst at high temperature and pressure. Nitrogen monoxide is then further oxidized to nitrogen dioxide (NO_2), which is finally absorbed in water to form nitric acid (HNO_3). This nitric acid can be reacted with certain bases or salts to produce various nitrate compounds such as sodium nitrate or potassium nitrate which are used as fertilizers [3]. The importance of industrial nitrate synthesis is driven by the need to increase agricultural production to meet global food demand. However, traditional synthesis methods such as the Haber-Bosch process for ammonia production and the Ostwald process for nitrate production require high energy consumption and contribute to greenhouse gas emissions, especially CO_2 and N_2O. This conventional industrial process combines nitrogen and hydrogen at high temperatures and pressures to produce ammonia, which can then be converted into nitrate [4]. However, this process is energy-intensive and produces large amounts of CO_2 emissions, as it uses steam reforming to extract hydrogen from natural gas (CH_4). This process consumes 1-2% of global energy and contributes to around 300 million tonnes of CO_2 emissions per year. The limitations of natural nitrate production and the environmental impact of conventional industrial methods have driven research into more efficient and environmentally friendly nitrate synthesis technologies [5]. This new technology is expected to be able to meet the agricultural demand for nitrate fertilizer without damaging the environment. Therefore, research and development of new, more environmentally friendly technologies have become an important focus. These efforts include the development of more efficient catalysts, the use of renewable energy sources, and electrochemical methods for nitrate synthesis. The goal is to reduce environmental impacts while still meeting the nitrogen needs of modern agriculture.

Air plasma electrolysis is the latest technology which is a development of air plasma technology, where plasma is formed in the liquid phase of the electrolyte solution with the help of electrical energy, so that the targeted nitrate compound can be directly in liquid form [6]. This method provides a much higher yield than conventional electrolysis due to the presence of radical compounds that play an extraordinary role in chemical reactions in solution [7]. This method is effective in encouraging the formation of radical compounds that help O_2 and N_2 gases as components of air to react with plasma to form nitrate compounds in the liquid phase. The working principle of making liquid nitrate fertilizer with plasma electrolysis is that air is injected into the electrolyte solution where plasma is formed. At this stage O_2 and N_2 from the air will react with plasma to form nitrate compounds, while hydrogen gas which is produced in large quantities from the plasma electrolysis process can react with N_2 to form ammonia [8]. A parameter that has never been done in the synthesis of liquid nitrate fertilizer using the plasma electrolysis method is the addition of Fe^{2+} ions which are important components in the plasma electrolysis process, because the ability of Fe^{2+} to change H_2O_2 formed due to recombination between •OH back into •OH (Fenton reaction) will increase the amount of •OH in solution [9]. The high •OH formed in solution will be able to increase nitrate formation [10]. For this reason, it is necessary to observe the parameters of the addition of Fe^{2+} ions and the optimization of Fe^{2+} concentration on its effect on nitrate formation. The next parameter is the initial pH of the solution against the time required for nitrate formation.

In the plasma electrolysis process, reactive oxygen and nitrogen (RONSs) are produced either with or without the addition of Fe^{2+}. RONSs are the main oxidizers used in the advanced oxidation process. These uncharged RONSs are formed due to the breaking of the paired electron bonds in a molecule. The RONSs formed (•H and •OH) are uncharged. RONSs OH will quickly recombine to form hydrogen peroxide (HO:OH) which is also uncharged. During the plasma electrolysis process, the number of free radicals, reactive species and oxidizer molecules formed, such as •OH, •H, •O and H_2O_2, is greater than the amount produced in conventional electrolysis [11]. The plasma electrolysis process causes a discharge that forms conductive channels so that the electrons with very high energy produced in water can ionize, dissociate and/or recombine water molecules [12].

2. Methodology
2.1 Materials

This research utilized various materials to facilitate plasma electrolysis and nitrogen fixation. Air injection gases acted as reactants, and a 0.02 M solution of potassium sulfate (K_2SO_4) from Merck (1.05153.0500) dissolved in distilled water served as the electrolyte. Nitrate concentration during the process was measured using the Nitrate Test Reagent HACH 2.106.169, and Iron (II) Hydroxide ($Fe(OH)_2$) from Merck (1.19781.0100) was also employed.

2.2 Experimental Setup

The experimental setup shown in Figure 1 featured a glass cylindrical reactor with a 1.2-liter capacity, equipped with a temperature sensor, condenser, and power analyzer. The electrode setup included a stainless steel cathode (AS SUS 316, DIA 5 mm) and a tungsten anode (EWTH-2 RHINO GROUND, 1.6 mm x 175 mm), with a 5 mm length and 27.13 mm² contact area submerged in the electrolyte solution. The tungsten anode, used as the anodic plasma electrode, was enclosed in a glass sheath to restrict its submerged contact area. A DC power supply, capable of delivering 0–1000 V and 0–5 A, powered the system, operated at 700 V and 400 W. Nitrogen and oxygen were injected at a flow rate of 0.8 L/min, while a temperature sensor monitored the process to maintain a maximum temperature of 60°C.

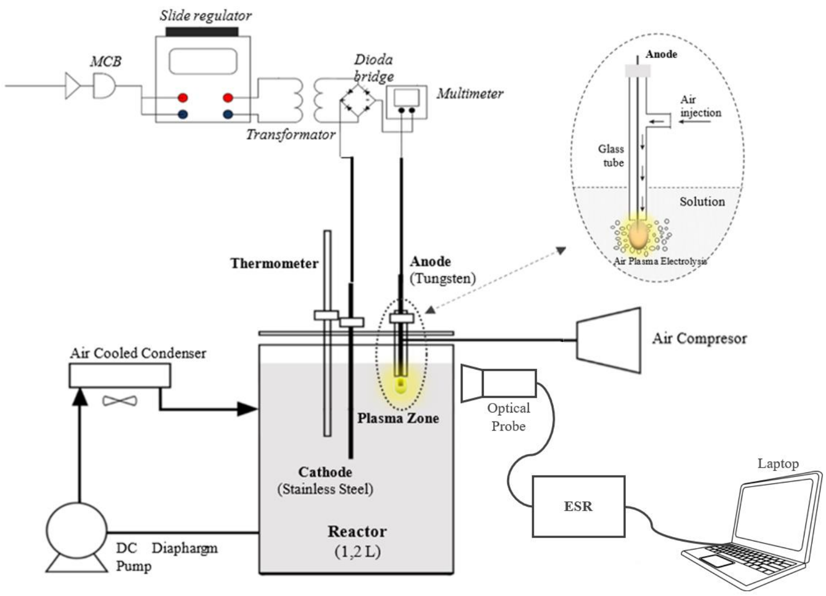

Fig. 1. Experimental set up of plasma electrolysis reactor

2.3 Procedure
2.3.1 Plasma setup

Before synthesizing liquid nitrate fertilizer using a plasma electrolysis reactor, it is crucial to first evaluate the reactor's performance. This involves testing to determine the characteristics of the plasma formed in the glow discharge zone within a specific voltage range. The test procedure includes incrementally increasing the voltage by 20 V, measuring the corresponding current, and recording the data. If the current value fluctuates, it is recorded over 1 minute, and the average is calculated. These measurements are used to generate a voltage-current curve based on the 20 V increments. The plasma characterization tests were conducted with an electrolyte concentration of 0.02 M K_2SO_4. The glow discharge zone is identified by observing a larger and more stable plasma, which occurs when the relationship between voltage and current becomes directly proportional.

2.3.2 Nitrate analysis

To measure total nitrate content, prepare 25 mL of the test sample in a 100 mL volumetric flask and add 5 g of Nitraver 5 Nitrate Reagent Powder Pillow (HACH 2106169), then shake thoroughly until dissolved. Pass the solution through a reduction column at a controlled flow rate of 7–10 mL/min to convert nitrate into nitrite. After adding the dye solution, measure the absorbance of the solution using a spectrophotometer set at a wavelength of 543 nm. This measurement should be taken between 10 minutes and 2 hours after the dye solution is added to ensure accuracy. The total nitrate content is then determined using a calibration curve, reflecting the nitrate reduced to nitrite during the process.The analysis setup for the plasma electrolysis process included two main pieces of equipment: UV-VIS Spectrophotometer (The BEL Engineering UV-M51 Single Beam Spectrophotometer) was used to measure concentrations of nitrate. This device enabled the detection of these key ions within the electrolyte solution, crucial for evaluating nitrate synthesis efficiency.

2.3.3 RONSs analysis

Electron Spin Resonance (ESR) Spectroscopy was employed to analyze the emission spectrum and detect gas formation in the reactor, a result of plasma discharge at the electrodes. The ESR system was equipped with an optical probe positioned in a dark room and operated within a wavelength range of 200–1100 nm, utilizing an ICCD (Intensive Charge-Coupled Device) camera for high-sensitivity detection. Spectral signals were recorded with a time resolution of 1 ms, and the data was processed using Maya 2000 Pro spectrometer software to produce semi-qualitative graphical representations of the emission spectra. This setup enabled detailed observation of the formation and emissions of Reactive Oxygen and Nitrogen Species (RONSs) during the plasma electrolysis process.

3. Results
3.1 The Effect of Initial pH=6 on Nitrate Production

The phenomenon of decreasing pH along with the formation of nitrate because nitrate compounds are acidic compounds and the pH has reached equilibrium [13]. The more acidic a solution is, the absorption capacity of NO_2 converted into NO_3 decreases and ultimately the concentration of nitrate decreases. When conditions become more acidic, based on Le Chatelier's

Principle, the equilibrium will shift to the left, namely the formation of nitrite while the concentration of nitrate decreases [14]. This equilibrium can be seen to occur when the pH approaches 3, the concentration of nitrate decreases due to the reverse reaction towards nitrite. Therefore, low pH conditions will cause the concentration of nitrate to decrease due to the equilibrium or reverse reaction towards nitrite [15].

Table 1 shows that the increase in nitrate production is quite significant in the 5th to 30th minute for the process without the addition of Fe^{2+} ions, then the concentration of nitrate produced begins to decrease in the 35th to 60th minute. The same thing happens in the formation of nitrate with the addition of Fe^{2+} ions, there is an increase in the 5th to 45th minute, then decreases in the 50th to 60th minute. This is thought to be caused by a reduction reaction of nitrate to nitrite which can interfere with the effectiveness of the reaction. The reduction reaction is thought to be caused by the nitrate that has been produced being exposed to UV from plasma [16]. Then when the nitrate concentration continues to decrease. This is because the pH conditions are getting smaller and smaller because they are influenced by the nitrate ions produced which are acidic. The more acidic a solution is, the weaker the ability to absorb NO_2 gas into NO_3 over time and ultimately causes the nitrate produced to be smaller. This is also supported by data on the decrease in pH from the beginning of the process (5th minute) to 60th minute. The more acidic a solution is, the less the absorption capacity of NO_2 converted into NO_3 and ultimately the nitrate concentration decreases. The phenomenon of decreasing pH can be seen in the reaction [16]:

$$3HNO_2 \leftrightarrow H^+ + NO_3^- + 2NO + H_2O \quad (1)$$

Table 1
Nitrate production

Time (minute)	Without Addition of Fe^{2+} ions		With Addition of Fe^{2+} ions (30 ppm)	
	pH	Nitrate Production (ppm)	pH	Nitrate Production (ppm)
5	6	1889	6	2024
10	5.8	2033	5.83	2367
15	5.71	2402	5.4	2463
20	5.22	2501	4.85	2543
25	4.88	2540	4.6	2675
30	4.62	2577	4.41	2785
35	4.3	2474	4.22	2795
40	4.01	2398	3.98	2804
45	3.92	2265	3.76	2808
50	3.8	2196	3.54	2695
55	3.71	2156	3.31	2554
60	3.6	2046	3.1	2432

In plasma electrolysis technology, hydrogen peroxide (H_2O_2) is produced in significant quantities due to the reaction of abundant hydroxyl radicals (•OH). This makes the application of *Fenton's reaction* highly compatible with the technology, as it leverages the surplus of •OH radicals generated during the synthesis of liquid nitrate fertilizers. Fenton's reaction involves the interaction between iron ions (Fe^{2+}) and hydrogen peroxide (H_2O_2), facilitating the regeneration of •OH radicals by decomposing H_2O_2 [17]. At an initial pH of 6, Fe^{2+} remains stable enough to interact with H_2O_2 via the Fenton reaction mechanism. This reaction produces hydroxyl radical (•OH), which is one of the most reactive RONSs. However, pH 6 is close to the optimal threshold for the Fenton reaction, where the efficiency of •OH formation is slightly reduced compared to pH 3 (ideal acidic conditions). At higher pH, Fe^{2+} tends to precipitate as $Fe(OH)_2$, reducing its effectiveness as a catalyst. The chemical interaction central to the Fenton reaction can be represented by the following equation:

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow Fe^{3+} + 2H_2O \quad (2)$$

In this reaction, Fe^{2+} ions interact with hydrogen peroxide, yielding hydroxyl radicals (•OH) and hydroxide ions (OH^-), while simultaneously oxidizing Fe^{2+} to Fe^{3+}. The highly reactive •OH radicals produced are pivotal in improving the efficiency of nitrate synthesis during plasma electrolysis. This process is pH-dependent, as the Fenton reaction occurs exclusively under acidic conditions, where •OH becomes the dominant reactive species. The oxidizing mechanism in Fenton's reaction can be categorized into two types: (1) chain reactions, which require only a minimal amount of reducing agent, and (2) non-chain reactions, where the overall oxidation process is governed by •OH production and depletion. In this reaction, Fe^{2+} ions interact with hydrogen peroxide, yielding hydroxyl radicals (•OH) and hydroxide ions (OH^-), while simultaneously oxidizing Fe^{2+} to Fe^{3+} [18]. The highly reactive •OH radicals produced are pivotal in improving the efficiency of nitrate synthesis during plasma electrolysis. This process is pH-dependent, as the Fenton reaction occurs exclusively under acidic conditions, where •OH becomes the dominant reactive species. The oxidizing mechanism in Fenton's reaction can be categorized into two types: (1) chain reactions, which require only a minimal amount of reducing agent, and (2) non-chain reactions, where the overall oxidation process is governed by •OH production and depletion [19].

$$Fe^{2+} + \bullet OH \rightarrow (Fe\text{-}OH)^{2+} \quad (3)$$

The efficiency of H_2O_2 decomposition reaches its optimum at an acidic pH of 3.5, as the hydrolysis reaction with Fe^{2+} ions create an extensive catalytic surface for H_2O_2. This accelerated decomposition greatly increases the generation of hydroxyl radicals (•OH). The inclusion of Fe^{2+} ions is particularly beneficial in plasma electrolysis technology for producing liquid nitrate fertilizers, due to the elevated production of •OH radicals [20].

3.2 The Reactive Oxygen and Nitrogen (RONSs) Species Production

In plasma, an initial pH of 6 provides a favorable environment for the formation of additional RONSs, such as nitrogen oxides (NOx), ozone (O_3), and peroxynitrite ($ONOO^-$), primarily through plasma-water reactions. The addition of Fe^{2+} accelerates oxidation-reduction reactions, increasing the formation of •OH and other species such as H_2O_2, which contribute to the production of RONSs. Plasma electrolysis at pH 6 creates mild-neutral conditions that allow RONSs generation to occur more stably without significant degradation. The addition of Fe^{2+} provides additional catalysis that accelerates the formation of RONSs, although the intensity is slightly lower compared to more acidic pH conditions.

The results of this study indicate that the formation of nitrate is influenced by reactive species in the form of N, N^{2*}, N^{2+}, •OH, •H and •O, especially reactive species nitrogen and •OH are needed to form nitrate from both the NO pathway and the ammonia pathway. The production of these reactive species affects the amount of nitrogen and oxygen injection into the plasma electrolysis reactor so that in this study the initial pH=6 is analyzed for its effect on nitrate formation. When plasma is generated in an electrolyte solution at atmospheric pressure, it produces high-energy electrons that can effectively ionize air molecules. Emissions of N^{2*}, •O and •OH were identified as dominant species in plasma generated in an electrolyte solution at atmospheric pressure. The formation of •O, •OH, •H in addition to injection is also produced by the dissociation of H_2O [21].

Figure 2, Figure 3 and Table 2 show the formation of RONSs with and without the addition of Fe^{2+} at initial pH = 6 which has high •OH and •O emission intensity. This is because the role of •O in the formation of •OH is in accordance with Eq. (4) [22].

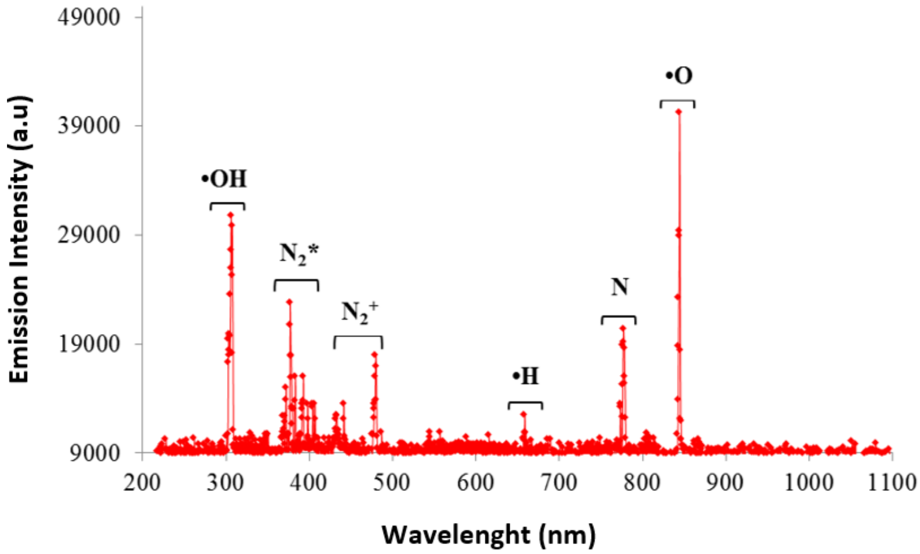

Fig. 2. Emission Intensity of RONSs without Addition of Fe^{2+} ions (initial pH=6)

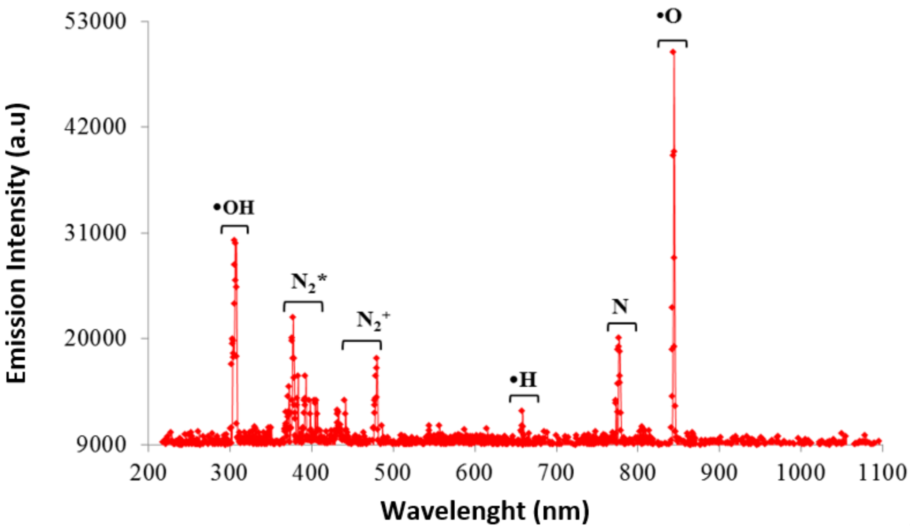

Fig. 3. Emisison Intensity of RONSs with 30 ppm of Fe^{2+} ions (initial pH=6)

Table 2
RONSs Production in initial pH=6

Plasma electrolysis process	Radicals emission intensity (a.u)						Nitrate(mg/L)
	N	N_2*	N_2^+	•OH	•H	•O	
Without addition of Fe^{2+} ions	20415	25782	22871	30287	12664	40356	2046
With 30 ppm Fe^{2+} ions	20139	28540	18023	30863	12547	49800	2432

radicals wavelenght : •OH (306 nm). •H (654 nm). •O (844 nm). N_2 (317 nm). N_2^+ (479 nm). N (777 nm)

$$•O + H2O(l) \rightarrow •OH + •OH \quad (4)$$

•OH species are reactive species with the highest oxidation state which can oxidize nitrogen from the air to nitrate. •OH is produced extensively by plasma due to gas ionization from the Joule heating effect of water from the solution. The role of reactive species •OH and •O according to Eq. (5) to Eq. (11) [23].

$$N_2 + e \rightarrow N + N + e \quad (5)$$

$$E + O2 \rightarrow •O + •O + e \quad (6)$$

$$N_2 + H_2O \rightarrow N_2^+ + •OH + •H \quad (7)$$

$$N_2 + •O \rightarrow NO + N_2^* \quad (8)$$

$$N_2^* + •O \rightarrow NO + N \quad (9)$$

$$N + •O \rightarrow NO_{(g)} \quad (10)$$

$$NO + •O \rightarrow NO_{2(g)} \quad (11)$$

This equation shows the role of •OH and •O in the formation of NO which will react with hydroxyl and oxygen radicals to form nitrite and nitrate. Another role is also in the formation of •OH and •H [24].

$$NO_2 + •OH \rightarrow HNO_3 \quad (12)$$

4. Conclusions

The addition of Fe^{2+} ions significantly enhances the production of Reactive Oxygen and Nitrogen Species (RONSs) during nitrate synthesis using a plasma electrolysis reactor. Fe^{2+} acts as a catalyst in the Fenton reaction, promoting the generation of hydroxyl radicals (•OH), a key reactive species in the process. Controlling the initial pH of the system influences the efficiency of RONSs production. At an initial pH of 6, the Fe^{2+} ions remain stable and effectively catalyze reactions that generate •OH radicals and other RONSs, though the efficiency is slightly lower compared to more acidic conditions (pH 3-4). The combination of plasma discharge and Fe^{2+} addition enhances the electrochemical reactions in the reactor, leading to a more efficient formation of nitrogen oxides (NOx), and hydroxyl radicals, which are crucial for nitrate synthesis. The increased RONSs production facilitated by Fe^{2+} ions under controlled initial pH conditions improves the overall efficiency of nitrate synthesis, making the process more effective and sustainable. The findings demonstrate the importance of Fe^{2+} addition and pH control as critical factors in optimizing nitrate synthesis via plasma electrolysis, paving the way for further advancements in sustainable fertilizer production.

Acknowledgment
Thank you to the Directorate of Research, Technology, and Community Service, Directorate General of Higher Education, Research, and Technology, Ministry of Education, Culture, Research and

Technology for the 2024 budget year through the Fundamental Research scheme funding Contract Number 127.12.6/UN37/PPK.10/2024.

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