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Hydroxyl Radicals Production in Nitrogen Fixation with Addition of Fe^{2+} Ions Using Plasma Electrolysis

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ABSTRACT

Nitrogen fixation using the Haber-Bosch process generates carbon dioxide emissions, so environmentally friendly alternative technologies are needed. Plasma electrolysis is recommended as a nitrogen fixation method that produces liquid nitrate because it does not generate emissions with raw materials from the natural air. The plasma electrolysis process generates hydroxyl radicals in the nitrate formation process. Thus, the aim of this research is to increase hydroxyl radicals by adding Fe^{2+} ions. The methods used include characterizing the current and voltage strength in the reactor to observe the glow discharge position for plasma formation. The analysis of hydroxyl radicals formed with the addition of Fe^{2+} ions was conducted using Electron Spin Resonance (ESR). The analysis of the yield of liquid nitrate formed was performed using a UV VIS Spectrophotometer. The results obtained were the emission spectrum of radicals formed in plasma without air injection. The wavelengths of the detected radicals are as follows: •OH (hydroxyl radical) at 306 nm, with an intensity of 21.696 a.u, •H (hydrogen radical) at 654 nm, with an intensity of 12.572 a.u. and •O (oxygen radical) at 844 nm, with an intensity of 13.267 a.u. When air injection is used, 0.8 liters per minute (lpm), there is a significant increase in the intensity of reactive species required for nitrate formation, such as excited nitrogen (N_2*) at 28540 a.u, hydroxyl radicals (•OH) at 30863 a.u, and oxygen (•O) at 49800 a.u. the concentration of nitrate produced reaches 1889 ppm. This is different from the condition without air injection (0 lpm), where nitrate is not formed.

1. Introduction

The atmosphere contains an abundant amount of free nitrogen, constituting 78% in the form of N_2, which is inert and does not easily react with other chemical elements to form new compounds [1]. However, plants cannot directly absorb nitrogen in the form of N_2. Therefore, nitrogen must be converted into a form that can be absorbed by plants, such as nitrate ions (NO_3^-) and ammonium ions

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(NH_4^+), through specific processes. This conversion can only be carried out by certain microorganisms capable of transforming free nitrogen in the air into a form usable by plants [2]. Denitrification is the process by which nitrate (NO_3) is gradually reduced to nitrite (NO_2), dinitrogen monoxide (N_2O), nitrogen monoxide (NO), and eventually to N_2 in anaerobic conditions. Several factors influence this process, such as high humidity, neutral pH (6.8 – 8.0), carbon availability, dissolved oxygen levels, and high temperatures. This process involves denitrifying bacteria, which are generally anaerobic. There are three groups of denitrifying bacteria: those that reduce NO_3 to N_2O, those that reduce NO_2 to N_2, and those that reduce NO_3 to NO_2, NO, and N_2O [3]. Denitrification can be detrimental in the use of fertilizers, including nitrate fertilizers, as nitrate, which is beneficial for plants, is converted back into nitrogen gas (N_2), which cannot be directly utilized by plants. Furthermore, N_2O gas produced during the process can damage the ozone layer [4]. Industrial nitrogen fixation via the conventional Haber-Bosch process has long been recognized as the main method for producing nitrogen-based fertilizers, particularly ammonia, by combining nitrogen and hydrogen at high temperatures and pressures. This process requires significant energy to perform steam reforming to obtain hydrogen gas from natural gas (CH_4), which also results in large amounts of CO_2 emissions [5]. The Haber-Bosch process is the most energy-intensive process in the chemical industry due to its high energy requirements. In addition to its role in fertilizer production, ammonia, which is produced through the HB process, is a crucial precursor for a wide range of chemicals, including paints and cleaning agents. This broad application explains the high global production of ammonia, which reached approximately 249.4 million tons. The process consumes around 1–2% of the world's energy and 2–3% of the global natural gas output, while contributing to the release of over 300 million metric tons of CO_2 annually. This significant environmental impact highlights the need for more sustainable alternatives to ammonia production [6].

The growing demand for fertilizers, high energy usage, and environmental concerns regarding CO_2 emissions from the nitrogen fixation industry have prompted the development of more sustainable, eco-friendly, and energy-efficient nitrogen fixation methods. Some alternatives explored include biological nitrogen fixation and the use of metal-complex catalysts under ambient pressure. Another promising technology to reduce environmental impact and improve energy efficiency is plasma electrolysis. Plasma is an ionized gas formed by electrical energy, allowing this process to significantly reduce reliance on fossil fuels while producing no gas emissions [7]. The Haber-Bosch process is an artificial nitrogen fixation method that converts free nitrogen into bound nitrogen to meet plant nitrogen needs. This process is widely used in chemical fertilizer production, where nitrogen gas from the air is reacted with hydrogen gas obtained from natural gas as a reactant, following the reaction Eq. (1) [8].

$$N_2 + 3H_2 \leftrightarrow 2\,NH_3 \tag{1}$$

The process takes place at high pressures of around 150-200 atm and high temperatures of approximately 500°C. The reaction is exothermic with ΔH = −92.4 kJ/mol [9]. An iron catalyst is used with the assistance of K_2O, CaO, SiO_2, and Al_2O_3. The use of a catalyst is essential due to the strong triple bond in nitrogen (N_2). Hydrogen for the process is obtained from natural gas (CH_4) through steam reforming, as described in Eq. (2) and Eq. (3) [10].

$$CH_4 + H_2O \leftrightarrow CO + H_2 \tag{2}$$

$$CO + H_2O \leftrightarrow CO + H_2 \tag{3}$$

Given the high energy consumption and harmful gas emissions associated with this process, along with the increasing demand for fertilizers, the development of alternative nitrogen fixation technologies that are more energy-efficient and environmentally friendly is necessary. Plasma electrolysis, as an eco-friendly technology, produces no gas emissions and significantly reduces dependence on fossil fuels [11]. Plasma electrolysis is an innovative technology developed from air plasma technology. In this method, plasma forms in the liquid phase of the electrolyte solution with the help of electrical energy, producing nitrate compounds directly in liquid form [12]. This technology has advantages over conventional electrolysis, yielding higher results due to the presence of radicals that play a significant role in the chemical reactions within the solution [13]. The method is effective in encouraging radical formation, which allows O_2 and N_2 gases, as the main components of air, to react with plasma to form nitrate compounds in the liquid phase [14]. The basic principle of liquid nitrate fertilizer production through plasma electrolysis involves injecting air into the electrolyte solution where plasma is formed. During this process, O_2 and N_2 from the air react with plasma to form nitrate compounds. Additionally, the hydrogen gas produced in large amounts during plasma electrolysis can react with N_2 to form ammonia [16]. One parameter that has not been extensively explored in nitrogen fixation using the plasma electrolysis method is the addition of Fe^{2+} ions. Fe^{2+} is an important component in this process due to its ability to convert H_2O_2, which forms from the recombination of hydroxyl radicals (•OH), back into hydroxyl radicals through the Fenton reaction. This process increases the concentration of hydroxyl radicals (•OH) in the solution, which in turn enhances nitrate formation [17]. High concentrations of hydroxyl radicals (•OH) in the solution are believed to increase nitrate production. Therefore, further research is needed to investigate the parameter of Fe^{2+} ions addition and its effect on hydroxyl radical production of nitrogen fixation using the plasma electrolysis process.

Previous research has discussed the basic mechanisms of plasma electrolysis in producing nitrate compounds, including the chemical reactions between N_2, O_2, and plasma in an electrolyte solution. This study discusses the basic mechanisms of plasma electrolysis to directly produce nitrate compounds from N_2 and O_2 gases in the liquid phase [18]. This research provides a scientific basis for the potential of plasma as an environmentally friendly technology for nitrogen fixation, but does not examine the effects of adding metal ions. Several studies have explored the role of hydroxyl radicals in plasma chemical reactions, including how these radicals affect the efficiency of the nitrate formation process [19]. This article explains the importance of hydroxyl radicals in plasma chemical reactions and their role in the nitrogen fixation process. Relevance: It shows that hydroxyl radicals are an important element in nitrate formation, but it has not yet focused on the method of enhancing it using Fe^{2+}. Fenton Reaction studies in other contexts (e.g., water treatment or organic compound degradation) show that Fe^{2+} can accelerate the formation of hydroxyl radicals through reactions with H_2O_2. However, the application of this concept in plasma electrolysis for nitrogen fixation has not been fully explained. This study will test the hypothesis that the addition of Fe^{2+} increases the concentration of hydroxyl radicals through the Fenton Reaction mechanism, which can enhance the efficiency of nitrate formation [20]. This study will test the hypothesis that the addition of Fe^{2+} increases the concentration of hydroxyl radicals through the Fenton Reaction mechanism, which can enhance the efficiency of nitrate formation. Previous research has shown that this method is more energy-efficient compared to conventional methods (such as Haber-Bosch), but factors that enhance reaction efficiency (such as the addition of certain metal ions) have been less discussed. By adding Fe^{2+}, this research will measure its direct impact on energy efficiency and nitrate productivity compared to conditions without Fe^{2+}.Previous research supports the theoretical and applicative relevance of plasma electrolysis as a nitrogen fixation technology, but the lack of exploration into the influence of Fe^{2+} ions in increasing hydroxyl radical (•OH) concentration and nitrate production efficiency creates a research gap. The new research has a strong justification to address this gap by utilizing the Fenton Reaction concept and validating its role in the context of plasma electrolysis.

2. Methodology

2.1 Materials

In this study, the plasma electrolysis and nitrogen fixation processes were carried out using various materials and equipment to ensure the efficiency and validity of the results. As the main reactants, nitrogen and oxygen gases are injected into the reactor to support the nitrogen fixation reaction, with a stable air flow rate of 0.8 L/min. The electrolyte solution used is a 0.02 M potassium sulfate (K_2SO_4) solution made by dissolving the material from Merck (1.05153.0500) into distilled water. Additionally, Fe^{2+} (Iron (II) Hydroxide ($Fe(OH)_2$) from Merck (1.19781.0100)) at a concentration of 30 mg/L is added to the electrolyte solution to support the electroplasma reaction. The nitrate test reagent HACH 2,106,169 is used to measure the concentration of nitrate formed.

2.2 Experimental Design

The process is carried out in a cylindrical glass reactor with a volume capacity of 1.5 liters, equipped with a temperature sensor, condenser, and power analyzer. This reactor is designed to maintain a maximum temperature of 60°C to avoid thermal degradation of the solution and ensure optimal conditions for plasma formation. As electrodes, a stainlesssteel cathode (AS SUS 316, diameter 5 mm) and a tungsten anode (EWTH-2 RHINO GROUND, 1.6 mm × 175 mm) are used, with the anode contact area limited to 27.13 mm² using a glass shield. This system is operated using a DC power supply with a capacity of up to 1000 V and 5 A, and in the experiment, the voltage is set at 700 V with a power of 400 W show in Figure 1.

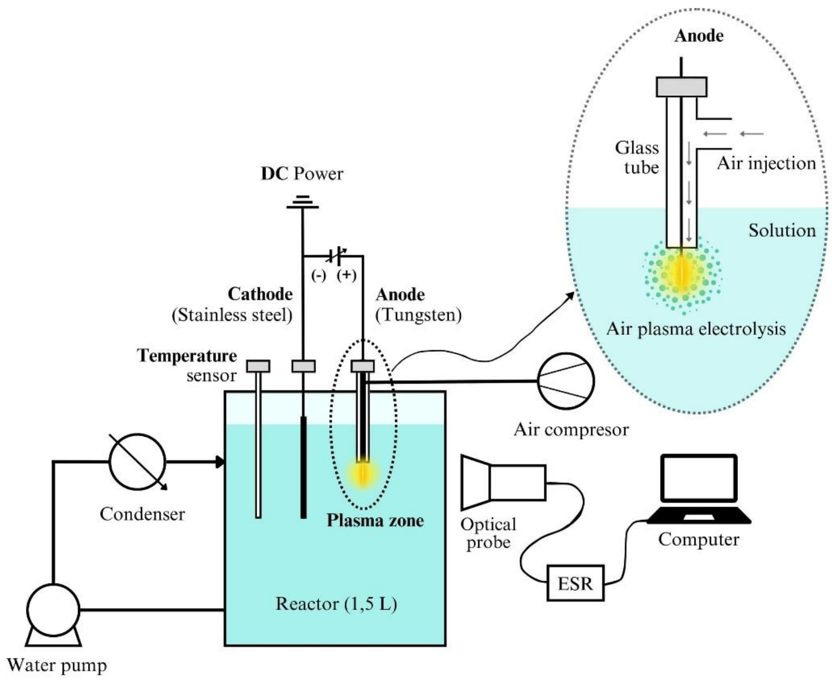


Fig. 1. Plasma electrolysis reactor setup

2.3 Procedure

The procedure begins with preparing an electrolyte solution containing 0.02 M K_2SO_4 and 30 mg/L Fe^{2+}, which is then introduced into the reactor. Nitrogen and oxygen gases are injected into the solution at a flow rate of 0.8 L/min, and the system is heated to a maximum temperature of 60°C.

After the initial parameters were set, the power supply was activated to start the plasma electrolysis process, producing visible plasma on the tungsten anode electrode. This process creates an electroplasma reaction that generates nitrate, nitrite, and ammonium.

2.4 Analysis

Analysis Equipment: UV-VIS Spectrophotometer (BEL Engineering UV-M51 Single beam spectrophotometer) was used to test for nitrate, nitrite, and ammonium concentrations. Electron Spin Resonance (ESR) Spectroscopy. This was used to analyze the emission spectrum and detect the formation of gases in the reactor due to plasma discharge at the electrodes. The ESR device was connected to an optical probe placed in a dark room, and it measured wavelengths from 200 to 1100 nm using an ICCD (Intensive CCD) camera. The signals were recorded with a time resolution of 1 ms, and the data was processed using the Maya2000 Pro spectrometer software to provide semi-qualitative graphical representations of the emission spectra. This experimental setup allows for a comprehensive analysis of the plasma electrolysis process, particularly focusing on nitrate synthesis and gas formation at the electrodes.

3. Result and Discussion

3.1 Electrolysis Plasma Process

Air plasma without air injection refers to a condition where plasma is formed solely using the gas or substances present in the system without the addition of external air. In this condition, the processes of ionization, dissociation, and excitation occur in the molecules or gases that are naturally available in the system, such as water vapor or existing gases. Figure 2 shows a plasma electrolysis process.

(a) (b) (c)

Fig 2. Plasma electrolysis process (a) without air injection (b) with air injection (c) with air injection and addition of Fe^{2+} ions

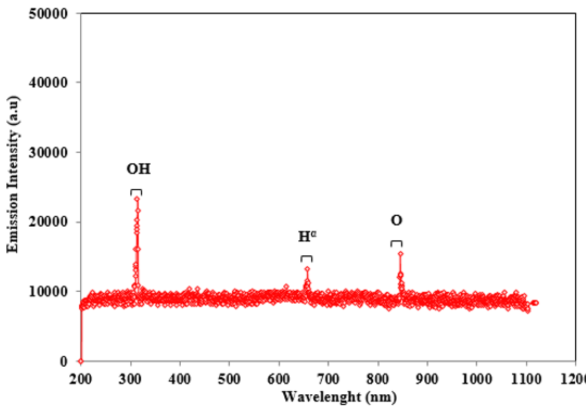
In Figure 2(a), without air injection, the gas composition in the plasma may be limited, which can affect chemical reactivity. The absence of nitrogen (N_2) from the air limits the production of nitrogen fixation in the form of nitrate or ammonia. However, in systems containing water or dissolved gas, the plasma process can still produce reactive oxygen or hydrogen compounds. In a system without air injection, plasma formation is typically driven by existing molecules or gases, such as water vapor (H_2O) or inert gases. Ionized and excited water molecules will break down into radicals •OH (hydroxyl), •H (hydrogen), and •O. (oksigen). Nitrogen fixation without air injection means that the plasma does not contain free nitrogen (N_2) from the atmosphere to interact with the plasma and form nitrogen compounds. Air or nitrogen gas injection is often required to ensure effective nitrogen fixation. Without air injection, plasma formation can be more limited because the number of components involved in the plasma reaction is fewer. The reaction between the formed radicals is also less compared to systems that have air injection, which provides more reactant gas [21]. In Figure 2 (b), the addition of gas in the form of air through a direct injection mechanism into the anode region can help initiate the ionization process in plasma formation. The injected air provides additional oxygen (O_2) and nitrogen (N_2) gas that can accelerate and enhance the ionization process. When these gases interact with the electric field around the anode, their molecules undergo dissociation and ionization, which then produces a very bright plasma. In Figure 2 (c), the addition of Fe^{2+} ions can affect plasma stability, depending on the concentration of the ions used. At the right concentration, Fe^{2+} ions can enhance plasma stability by strengthening the interactions between charged particles in the plasma, resulting in a more stable and reactive plasma. Fe^{2+} can mediate reactions between N_2 and O_2 with the plasma, producing various nitrogen oxide compounds (NO, NO_2) and nitrate (NO_3^-). Fe^{2+} ions play a role in lowering the activation energy of the reactions, accelerating the formation of desired nitrogen products, such as nitrate or ammonia [22].

The results depicted in Figure 2(a) reveal that the absence of air injection significantly limits nitrogen fixation capabilities. In such a system, the plasma relies solely on available molecules, such as water vapor (H_2O) or inert gases, to produce reactive species like hydroxyl radicals (•OH), hydrogen radicals (•H), and oxygen radicals (•O). The absence of free nitrogen (N_2) restricts the formation of nitrogen compounds, such as nitrates or ammonia, as the primary reactants are unavailable. This aligns with studies by Bogaerts et al. (2020) and Chen et al. (2021), which confirm that plasma systems operating without nitrogen-rich feed gases generate predominantly oxygen-based reactive species. These findings underline the challenges of achieving effective nitrogen fixation in systems without external nitrogen sources [23,24].

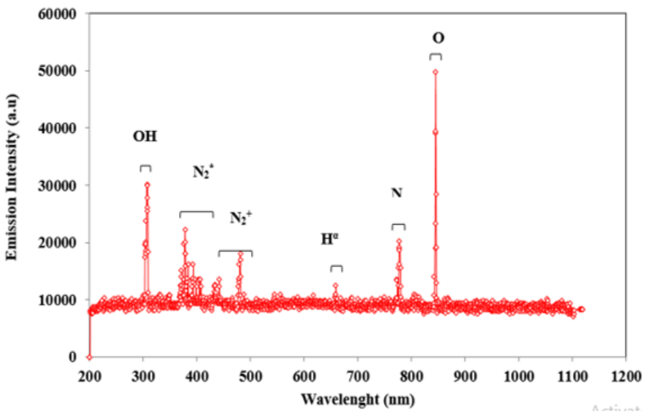
The introduction of air injection, as shown in Figure 2(b), significantly enhances plasma formation by providing nitrogen (N_2) and oxygen (O_2) gases directly into the anode region. These gases undergo dissociation and ionization under the influence of the electric field, producing a bright and highly reactive plasma. The availability of additional reactants leads to the formation of nitrogen oxides (NO, NO_2) and nitrates, which are critical for nitrogen fixation. This observation is consistent with the findings of Nayak et al. (2021), who demonstrated that air injection improves plasma activity and nitrogen oxide yields [25]. Sarma et al. (2020) reported similar enhancements in plasma reactivity when controlled air injection was applied, highlighting the importance of optimizing gas flow rates, as was done in this study with a precise rate of 0.8 L/min [26]. However, Chen et al. (2022) noted that excessive air injection could destabilize plasma, underscoring the importance of maintaining optimal conditions, which this research successfully addresses [27]. The addition of Fe^{2+} ions, as demonstrated in Figure 2(c), plays a pivotal role in enhancing plasma stability and reactivity. Fe^{2+} ions act as a catalyst, lowering the activation energy required for reactions between nitrogen (N_2) and oxygen (O_2), thereby accelerating the formation of nitrogen compounds such as nitrates and nitrogen oxides. This catalytic effect strengthens the interactions between charged particles in the plasma, resulting in a more stable and efficient reaction environment. These findings are consistent with research by Zhang et al. (2018) and Jiang et al. (2023), which highlighted the importance of transition metal ions, including Fe^{2+}, in facilitating plasma-based nitrogen fixation [28, 29]. The stabilizing effect of Fe^{2+} ions ensures that the plasma remains reactive over extended periods, contributing to higher product yields. The comparative analysis indicates that systems without air injection are inherently limited in their ability to fix nitrogen due to the absence of essential reactants. In contrast, air injection significantly enhances the plasma's reactivity by introducing N_2 and O_2, key components for nitrogen fixation. Additionally, the inclusion of Fe^{2+} ions not only stabilize the plasma but also accelerates reaction rates, leading to improved yields of nitrogen products. These results align with existing studies and provide a deeper understanding of how these factors interact to influence plasma behavior and reaction outcomes.

3.2 Hydroxyl Radicals Production

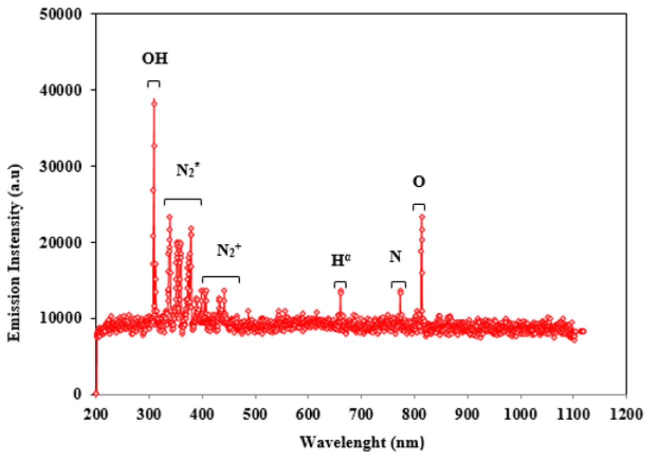
Based from Figure 3 (a), the emission spectrum of radicals formed in plasma without air injection. The wavelengths of the detected radicals are as follows: •OH (hydroxyl radical) at 306 nm, with an intensity of 21.696 a.u, •H (hydrogen radical) at 654 nm, with an intensity of 12.572 a.u. and •O (oxygen radical) at 844 nm, with an intensity of 13.267 a.u. The formation of these radicals (•OH, •H, and •O) originates from water molecules undergoing dissociation, ionization, and excitation through vibrational and rotational energy processes.



(a)



(b)



(c)

Fig. 3. Emission intensity of radical production (a) without air injection (b) with air injection (c) with air injection and addition of Fe^{2+} ions

These reactions highlight the interaction between water molecules and the energy supplied by the plasma, which results in the breakdown and excitation of water into various reactive radicals.

Dissosiation:
$H_2O + e \rightarrow \bullet OH + \bullet H + e$ (4)

Ionisation:
$H_2O + e \rightarrow 2e + H_2O^+$ (5)
$H_2O+ + H_2O \rightarrow \bullet OH + H_3O^+$ (6)

Extacion with vibration/rotation:
$H_2O + e \rightarrow H_2O^* + e$ (7)
$H_2O^* + H_2O \rightarrow H_2O + \bullet OH + \bullet H$ (8)
$H_2O^* + H_2O \rightarrow H_2 + \bullet O + H_2O$ (9)
$H_2O^* + H_2O \rightarrow 2\bullet H + \bullet O + H_2O$ (10)

The nitrogen and oxygen content of the air that is injected into the electrolyte solution, which is the primary raw material for nitrogen fixation and yields liquid nitrate, is depicted in image 3(b). Plasma is formed in the process of anodic plasma electrolysis through the formation of a gas sheath around the anode, which acts as a barrier to the flow of electrons and triggers the occurrence of electrical discharge in the form of plasma. One of the mechanisms for the formation of this gas sheath is through the evaporation of water caused by the Joule heating effect. When electric current flows through the electrolyte solution, the water around the anode heats up, causing water molecules to evaporate and form a gas layer that envelops the anode surface. This gas layer creates resistance to electron flow and establishes conditions that support the formation of plasma. In addition to water evaporation, a gas sheath can also form through the injection of external gases, such as air, around the anode. This air injection introduces gases like nitrogen (N_2) and oxygen (O_2) into the process, thereby reducing the energy required for water evaporation and accelerating plasma formation. When the gas sheath forms, the electric field around the anode becomes stronger due to the obstruction of electron flow, which ultimately triggers the occurrence of electrical discharge. Nitrate formation is impacted by the production of •OH by plasma. Apart from hydroxyl radicals, other reactive species including N, N^{2*}, N^{2+}, •H, and •O are also formed during emission intensity experiments involving nitrogen and oxygen injection [30].

This process increases the number of free radicals such as •O, •N, and •OH, which play a role in chemical reactions within the plasma. Additionally, air injection can also expand the plasma volume and enhance the efficiency of forming desired compounds, such as nitrate or ammonia, depending on the intended application in the plasma reaction. In Figure 3 (c), the addition of Fe^{2+} ions to the plasma flame can have several significant effects on the dynamics and chemical reactivity within the plasma. The Fe^{2+} ion acts as a catalyst that aids in various chemical reactions, particularly through the famous *Fenton reaction* mechanism, which enhances the formation of reactive radicals such as hydroxyl radicals (•OH). The presence of the Fe^{2+} ion increases the overall reactivity of the plasma. The Fe^{2+} ion can help accelerate reactions involving dissociation and ionization, facilitating the formation of reactive species such as oxygen radicals (•O) and nitrogen radicals (•N), which are crucial in plasma processes, such as nitrogen fixation and nitrate formation. One of the challenges faced in this technology is the potential of hydroxyl radicals to react with each other, producing hydrogen peroxide (H_2O_2). This reaction can reduce the concentration of available •OH radicals, thereby decreasing the efficiency of plasma electrolysis technology. The addition of iron ions (Fe^{2+})

can be an effective solution through the principle of the Fenton reaction. In the Fenton reaction, Fe^{2+} ions react with the formed H_2O_2, converting it back into hydroxyl radicals (•OH) and increasing the number of radicals available in the solution.

$$H\bullet + H\bullet \rightarrow H_2 \quad (8)$$
$$H\bullet + \bullet OH \rightarrow H_2O \quad (9)$$
$$\bullet OH + \bullet OH \rightarrow H_2O_2 \quad (10)$$
$$\bullet OH + H_2O_2 \rightarrow HO_2\bullet + H_2O \quad (11)$$
$$\bullet OH + HO_2\bullet \rightarrow H_2O + O_2 \quad (12)$$

In plasma electrolysis technology, the production of hydrogen peroxide (H_2O_2) is quite high because it is a result of the reaction between hydroxyl radicals (•OH) that are generated in large quantities. The application of *Fenton's reaction* is very suitable for this technology because it can take advantage of the excess •OH radicals formed during the synthesis process of liquid nitrate fertilizers. Fenton's reaction, which involves the interaction between iron ions (Fe^{2+}) and hydrogen peroxide (H_2O_2), helps to regenerate the amount of available •OH radicals by decomposing H_2O_2 [31]. The reaction between iron ions (Fe^{2+}) and hydrogen peroxide (H_2O_2) in the Fenton reaction can be written as follows:

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow Fe^{3+} + 2H_2O \quad (13)$$

In this reaction, Fe^{2+} ions react with hydrogen peroxide, producing hydroxyl radicals (•OH) and hydroxide ions (OH^-), while oxidizing Fe^{2+} ions to Fe^{3+}. The •OH radicals generated from this reaction are highly reactive and play a crucial role in enhancing the efficiency of nitrate formation in plasma electrolysis. This equation can be analyzed to show that the Fenton reaction is influenced by the pH of the solution. The reaction can only occur under acidic conditions, where •OH becomes a reactive and dominant compound.The oxidizing ability using Fenton's reaction can be divided into two groups: (1) chain reactions, which require only a small amount of reducing agent, and (2) non-chain reactions, where the entire oxidation reaction is influenced by •OH and the loss of •OH.

$$Fe^{2+} + \bullet OH \rightarrow (Fe\text{-}OH)^{2+} \quad (14)$$

The decomposition ability of H_2O_2 reaches its maximum at an acidic solution pH of 3.5. This event can occur because the hydrolysis reaction by Fe^{2+} ions provides a large catalytic active surface for H_2O_2. The rapid decomposition ability of H_2O_2 will significantly enhance the production of •OH. The addition of Fe^{2+} ions is very beneficial for plasma electrolysis technology in the synthesis of liquid nitrate fertilizers due to the high yield of •OH. The following is the mechanism of the decomposition reaction of H_2O_2 with the addition of Fe^{2+} ions.

3.3 Nitrate Production

Table 1 shows that under conditions with an air injection of 0.8 liters per minute (lpm), the concentration of nitrate produced reaches 1889 ppm. This is different from the condition without air injection (0 lpm), where nitrate is not formed.

Table 1
Nitrate production

Plasma electrolysis process	Radicals' emission intensity (a.u)						Nitrate(mg/L)
	N	N_2*	N_2^+	•OH	•H	•O	
Without air	-	-	-	20012	10121	10245	-
Air injection 0.8 L/min	20139	28540	18023	30863	12547	49800	1889
Air injection 0.8 L/min + Fe^{2+} ions	12530	22655	11990	38320	12486	23670	2024

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

The formation of nitrate requires the presence of nitrogen (N_2) and oxygen (O_2), or at least one of them[x]. Without air injection (0 lpm) and without O_2 injection, reactive species such as nitrogen (N), excited nitrogen (N_2*), and nitrogen ions (N_2^+) are not formed, even though the emission intensity of hydroxyl radicals (•OH), hydrogen (•H), and adsorbed oxygen (•O) without air injection reaches 20012 a.u, 10121 a.u, and 10245 a.u, respectively. On the contrary, when air injection is used, there is a significant increase in the intensity of reactive species required for nitrate formation, such as excited nitrogen (N_2*) at 28540 a.u, hydroxyl radicals (•OH) at 30863 a.u, and oxygen (•O) at 49800 a.u. The presence of oxygen atoms generated from the ionization of O_2 by high-energy electrons can bond with reactive nitrogen species originating from the solution, forming nitrogen monoxide (NO) compounds. Subsequently, NO is oxidized to nitrogen dioxide (NO_2) and nitrate (NO_3^-), which are the end products of this process [32].

4. Conclusion

The advantage of plasma electrolysis technology is that it can produce a large amount of hydroxyl radicals (•OH), which can contribute to the synthesis of liquid nitrate fertilizers. However, there is a potential for these hydroxyl radicals to react with each other, resulting in the formation of hydrogen peroxide (H_2O_2). This reaction can reduce the performance of plasma electrolysis technology due to the decrease in •OH concentration. This issue can be addressed by adding Fe^{2+} ions based on the principle of the Fenton reaction.

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