

Synthesis of nitrates by atmospheric microplasma over water

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Abstract: Nitrates and nitrites are synthesized by DC microplasma directly in a solution of 1mM of NaCl. The liquid phase is characterized by ionic chromatography and gas phase by optical emission spectroscopy and mass spectroscopy. A linear trend is observed with the treatment time and the current. After the plasma treatment, disproportionation is observed but another species is involved in the conversion of nitrites into nitrates. In the gas phase, only nitric oxide is detected.

Keywords: Plasma agriculture, nitrates, microplasma

1. Introduction

Microplasmas have attracted a great interest for a number of potential applications such as nanoparticles synthesis [1], VOCs destruction [2], UV radiation sources [3] or medicine [4]. The reduction of the size of the plasma allows to maintain low gas temperature at high pressures and therefore shows a non-equilibrium chemistry at near ambient conditions [5,6]. The microplasma can be coupled with liquid surfaces to take advantages of the non-thermal operation at atmospheric pressure.

During the past few years, new approaches to synthesize fertilizers are being studied to increase food production and processing in order to meet the global demand for nutritional intake. One solution is the use of atmospheric plasma to produce nitrates to feed and give nutrients to plants. In fact, when aqueous solutions are treated by plasma, in air environment, several reactive oxygen and nitrogen species are generated [7-10]. Atmospheric plasma appears as an ecofriendly approach and can be easily coupled with green energy sources. A local production of pure nitrates fertilizers directly available in the flowing water feeding system can be used for some applications such as hydroponics or urban agriculture. In this study, the same philosophy as for the ozone process is applied: taking advantage of the composition of natural air in order to synthesize nitrates directly into water. The formation mechanism of nitrates (NO_3^-) is investigated in DC atmospheric microplasma. The solution is analyzed by ion chromatography, pH-meter and UV-visible spectrometry. The gas phase is analyzed by optical emission spectroscopy and mass spectrometry.

2. Experimental

Nitrates synthesis was performed in a setup presented in Fig. 1. An atmospheric-pressure microplasma was ignited at the liquid surface (1mM NaCl solution) in a flow of 25 $\text{ml}\cdot\text{min}^{-1}$ argon or air from a pressurized stainless steel capillary tube with a inner diameter of 0.2; 0.5 or 0.76 mm. The tip was positioned approximately 1 mm above the surface. A platinum wire immersed in the solution served as the counter electrode. The microplasma was ignited and sustained by a ballasted DC power supply. The discharge current was varied between 1 and 10 mA by adjusting the applied voltage. No stirring was applied in order to avoid disturbing the solution surface which was found to disturb the discharge.

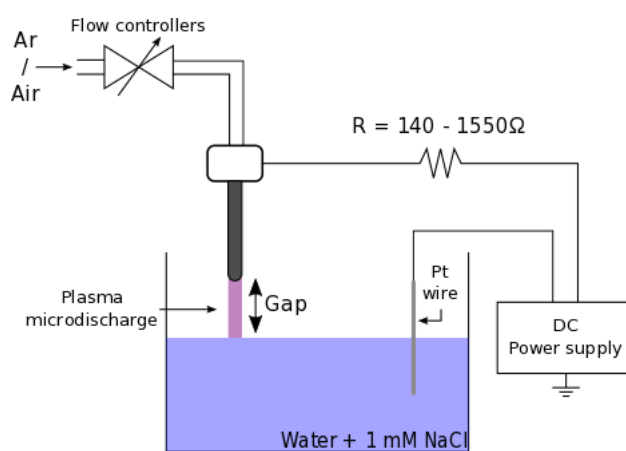


Fig 1. Schematic setup of DC microplasma

To control the atmosphere, the setup was put in a close reactor. The reactor atmosphere is pumped twice until reaching the pressure of 40 Torr and air or argon is injected in the reactor after each pumping at 5 $\text{L}\cdot\text{min}^{-1}$.

3. Results

After the plasma treatment, two species are detected by ionic chromatography in the liquid phase: nitrites and nitrates.

First, the influence of the gas, current and treatment time are investigated. The amount of nitrates is higher when air is used and a linear increase of the concentration is observed when increasing treatment time or current.

The liquid phase is analysed during time after the plasma treatment. Nitrites are known to disproportionate at a pH of 3.5 or under [11] in nitrates and nitric oxide according to the equation:



After the plasma treatment, the pH of the solution is at 3.5 or under, therefore, disproportionation is possible. As observed on the Fig 2., there is a conversion of nitrites into nitrates after the plasma is turned off.

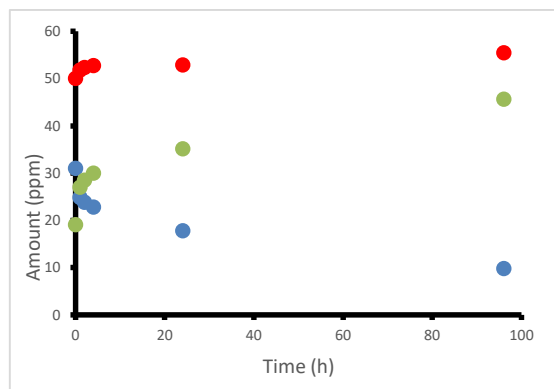


Fig 2. Conversion of nitrites into nitrates after the plasma treatment. The amount of Nitrites is presented in blue, the amount of nitrates is presented in green and the amount of NO_x^- is presented in red (NO_x^- represents the sum of NO_2^- and NO_3^-)

Disproportionation is a possible explanation of the conversion of nitrites but other species can also be involved in the process. The comparison between the solution after the plasma treatment and a solution of nitrites and nitrates without plasma treatment at a pH of 3 shows that another specie could be involved in the conversion.

When a plasma is ignited over water, hydrogen peroxide (H_2O_2) is synthesized [12] and it can oxidize nitrites to form nitrates during the treatment and after. Its role is investigated by using sodium pyruvate that traps H_2O_2 and radicals during the plasma treatment. Fig 3. shows that the quantity of nitrates decreases when the concentration of sodium pyruvate increases. The same trend is observed with the amount of nitrites. This could be explained by the fact that NO_2^- also can be formed through the reaction of H_2O_2 with NO.

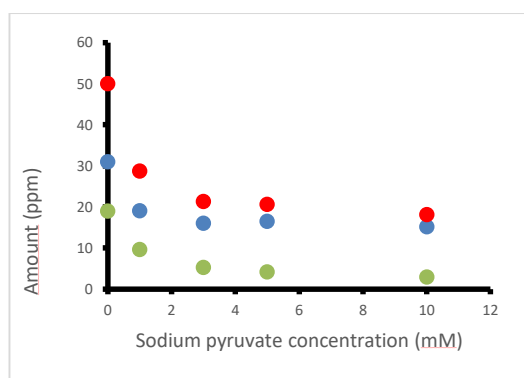
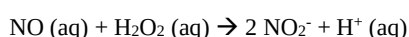


Fig 3. Amount of nitrites (in blue), nitrates (in green) and NO_x^- (in red) after 10 min of plasma treatment of a solution of variable concentration in sodium pyruvate

The philosophy of the process is the use of N_2 and O_2 from the air to synthesize nitrates. The plasma could

dissociate those compounds into atomic nitrogen and oxygen that can react together to form several nitrogen oxides. Other routes could involve vibrational excitation and dissociation. Two main intermediate oxides could be involved in the formation of nitrates: nitric oxide (NO) and nitrogen dioxide (NO_2). Mass spectrometry and optical emission spectrometry are performed on the plasma phase (see Fig 4.).

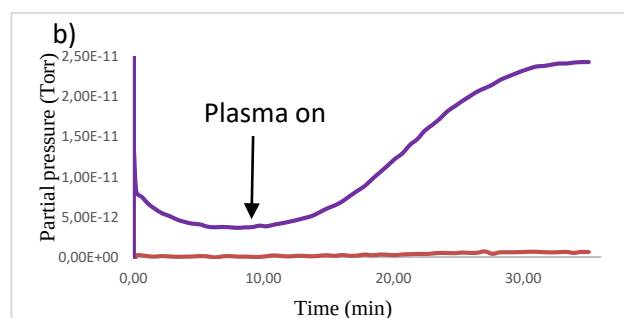
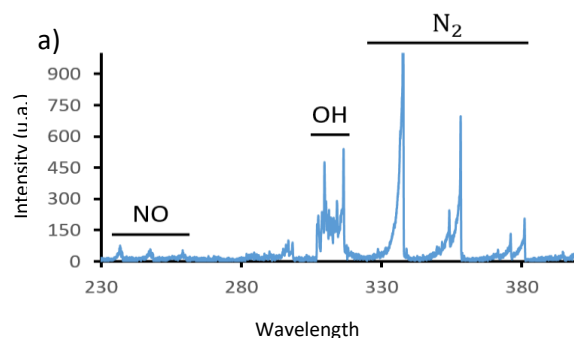
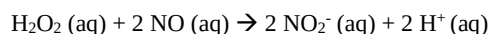
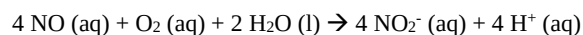


Fig 4. (a) Optical emission spectroscopy of the plasma over a solution of 1mM NaCl after 5 min of treatment. (b) mass spectrometry of the gas phase during the plasma treatment, NO in purple and NO_2 in red

From Fig 4. only NO is formed in the gas phase during the process and nitric oxide can be dissolved into the solution to form nitrites and nitrates in the solution. NO can react with H_2O_2 or O_2 to form nitrates following these reactions:



4. Conclusions

Nitrates can be synthesized directly in water by using a DC microplasma over an aqueous solution. The mechanism is supposed to start with N_2 and O_2 from the air which can react to form NO in the gaseous phase. The nitric oxide will dissolve in the solution to react potentially with H_2O_2 and O_2 in the solution to form nitrites. After that, nitrites could react with H_2O_2 to form nitrates. After the treatment, nitrites could disproportionate to form nitrates under acidic conditions ($\text{pH} < 3.5$). During the first couple of hours after the treatment another species, potentially H_2O_2 , is involved.

The quantity of nitrites and nitrates formed is linearly dependent on the treatment time and the current but there is no influence of the gap between the needle and the solution.

Further investigations are pursued in the plasma phase, including by FTIR, to better probe all intermediate species above the water solution.

5. References

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