Physicochemical Properties and Time Stability of Plasma Activated Water by a Liquid-Cathode Glow-Type Discharge in Air: The Effect of Air Confinement

Brenda Santamaría, Matías G. Ferreyra, Juan C. Chamorro, Ezequiel Cejas, Brenda L. Fina, and Leandro Prevosto

***Abstract*— Nonthermal discharges in atmospheric pressure air in contact with water produce large amounts of reactive species in the gas phase that can enter into the water by diffusion, thus inducing the formation of secondary reactive species in the liquid phase, including those long-lived species such as NO_2^-, NO_3^-, and H_2O_2. Depending on the controllable parameters of the discharge, the plasma activated water (PAW) may acquire different physicochemical properties, resulting in various applications. Physicochemical measurements of PAW obtained by means of a water-cathode glow-type discharge in atmospheric pressure air operating in open and closed reactor conditions are reported. The discharge was operated in a millisecond pulsed-dc regime at an rms current value of 100 mA and a power of 100 W. A large volume of 1 L of distilled water was treated for 30 min. In both cases, low pH values of ∼2.5 and very high levels of NO_3^- (up to 250 mg/L) in PAW were obtained; however, in the closed system, no H_2O_2 was found and high concentrations of nitrite (120 mg/L) were measured, while in the open system, large levels of H_2O_2 were observed (45 mg/L) and no NO_2^- was found. Likewise, the electrical conductivity value for the closed reactor (≈2000 μS/cm) was significantly higher than for the open reactor (≈1000 μS/cm). The reasons for these different behaviors in terms of PAW chemistry are discussed. Also, the time stability of PAW was measured.**

***Index Terms*— Nonthermal discharges, plasma activated water (PAW), reactive species in water.**

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I. Introduction

PLASMA is a partially or fully ionized gas consisting of a mixture of electrons, ions, and neutral particles, where the amount of positive and negative charges must balance. The most common mode of plasma generation at laboratory scale is by means of the use of electrical discharges in a gas [1], and they are traditionally divided into two broad categories: 1) thermal discharges—the energies of the heavy particles are of the order of the electron energy (∼1 eV = 11600 K) [2]—and 2) nonthermal discharges—the electron energy is much higher (∼1–3 eV) than the energy of heavy particles (∼300–1000 K) [3].

In recent years, interest in nonthermal discharges in (and in contact with) liquids has been increasing due to their multiple technological applications, covering areas such as nanomaterial deposition, medicine, environmental care, and agriculture, among others [4], [5], [6]. With respect to environmental care, given its ability to decompose organic and inorganic compounds in water, the use of nonthermal plasmas has focused on the degradation of dyes used in various industrial sectors, which are often resistant to traditional treatment processes [7], [8].

Within plasmas in agriculture, the utilization of nonthermal discharges through liquids that have previously been exposed to plasma [such as plasma "activated" water (PAW)] [4] has been focused on seed germination and plant fertilization, pathogen inhibition, and agrochemical degradation, among others [9]. This type of treatment, commonly called "indirect," has certain advantages over "direct" treatment (where substrates, such as seeds and food, are directly exposed to the discharge), such as the possibility of decoupling the PAW generation site from the application site, as well as the possibility of easily applying it on substrates with complex shapes.

A variety of nonthermal discharges have been used for PAW generation, such as gliding arc, dielectric barrier discharge (DBD), plasma jet, corona discharge, and glow discharge. The composition of the PAW depends on various operating parameters of the discharge, such as type of discharge, type of gas where the discharge is set, and plasma exposure

time, whether the discharge is set above or below the water surface, among others [9]. In air or similar mixtures, the main species found in water are reactive oxygen and nitrogen species (RONS), including hydroxyl radical, ozone, superoxide radical, peroxynitrite, nitrate, nitrite, and hydrogen peroxide. The latter three species—nitrate (NO_3^-), nitrite (NO_2^-), and hydrogen peroxide (H_2O_2)—have the longest half-lives in the liquid volume [9], although degradation time scales vary strongly depending on the pH [10].

A widely used nonthermal discharge in contact with liquids is the glow-type discharge. In air (or other molecular gases) at atmospheric pressure, the discharge becomes strongly inhomogeneous due to the plasma constriction, but the degree of thermal nonequilibrium is still maintained at high level [9], resulting in large amounts of RONS [3]. The RONS formed in the gas phase enters the liquid by diffusion, thus leading to the formation of reactive species in the volume of the liquid such as NO_3^-, NO_2^-, H_2O_2, and hydroxyl radical ($OH^{\cdot}$). The cathode voltage drops reported for water-cathode glow discharges are higher than their corresponding values for metal electrodes; this is because the secondary electron emission coefficient of water is 2–3 orders of magnitude lower than that of a metal cathode [11].

Despite the great interest and importance for practical purposes, at present, there have not been too many works characterizing the synthesis of large volumes of PAW (of the order of 1 L) by means of high-power discharges in air (and other gases) [12], [13], [14]. This work is an effort to address this issue.

Physicochemical experimental data of distilled water exposed to a nonthermal high-power glow-type discharge in atmospheric pressure air with the water being the cathode are reported. The volume of water treated was 1 L, while the maximum plasma exposure time reached 30 min. Two variants (treatments) were employed for the same experimental setup: 1) with the gaseous chamber where the glow discharge is set confined (closed reactor) and 2) with the open chamber (open reactor). In particular, pH values, electrical conductivity, and aqueous phase concentrations of NO_3^-, NO_2^-, and H_2O_2 are reported. Also, the time stability of PAW up to three months was measured.

II. Plasma Reactor

A schematic of the plasma reactor is presented in Fig. 1. A photograph of the discharge with liquid cathode is also shown. A pin-to-water electrode configuration was used, with a gaseous gap ≈10 mm. A needle shape (a tip radius of about 200 μm) of thoriated tungsten metal electrode (anode) was placed above the water to be treated, which was contained in a grounded reservoir of 1-L capacity made of AISI 304.

In order to increase the gas–liquid exchange surface and improve the mixing of the species that enter in the liquid volume, a vortex was generated with a magnetic stirrer. This also allowed the evaporation processes in the cathode spot to be negligible. In this sense, to avoid heating the PAW, the temperature of the water during the activation process

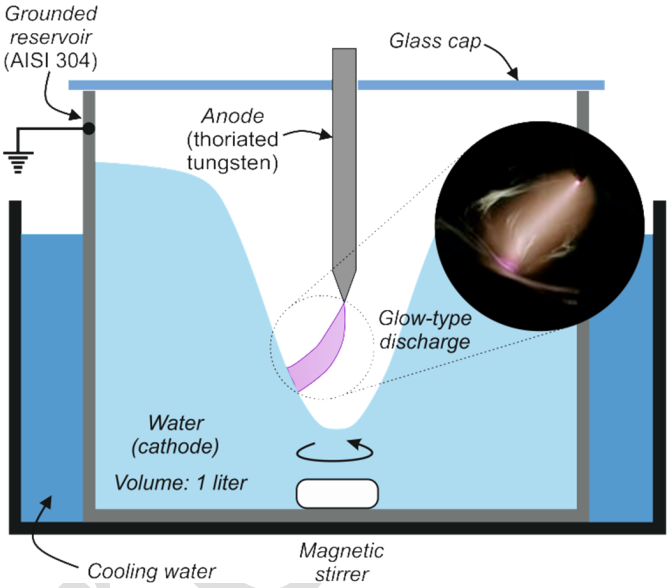

Fig. 1. Experimental arrangement. A photograph of the discharge is shown in the inset.

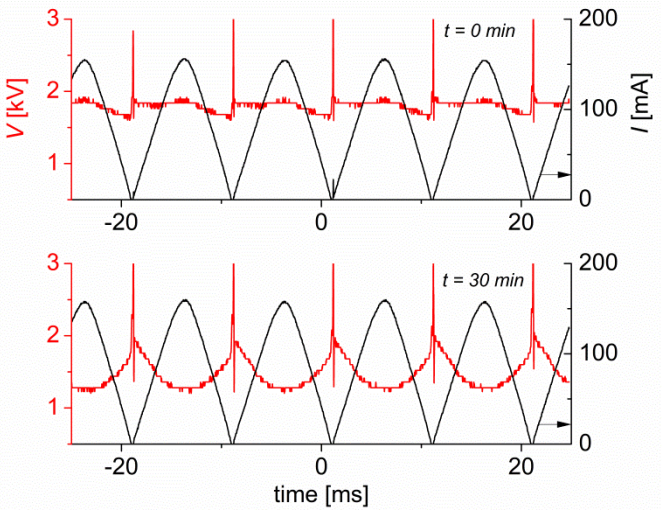

Fig. 2. Voltage (V) and current (I) oscillograms for $t = 0$ min and $t = 30$ min.

was kept constant at about 20 °C by means of a cooling system, due to the thermally fragile chemistry of H_2O_2 [14]. No significant changes in PAW volume were observed after the synthesis (<5 mL).

The power supply was a high-voltage transformer (25 kV, 50 Hz) with a high dispersion reactance (65 ± 2 kΩ). The output of the transformer was connected to the reactor through a semiconductor full-wave rectifier to define the polarity of the electrodes. The voltage and current signals were recorded through a four-channel oscilloscope (Tektronix TDS 2004C, sampling rate 1 GS s^{-1}, bandwidth 70 MHz) by using a resistive–capacitive voltage divider (Tektronix P6015A, 1000X, 3 pF, 100 MΩ) and a low-inductance shunt resistance (100 Ω), respectively.

Fig. 2 shows the voltage (V) and current (I) oscillograms at the beginning ($t = 0$ min) and after 30 min of water activation

(t = 30 min). The discharge is likely ignited by a streamer-to-spark high-voltage transition (voltage spikes up to ∼8 kV are found at the beginning of each pulse) [5]. A transient positive corona discharge (cathode-directed streamer development) is formed near the metal pin electrode before sparking, but soon after the breakdown, the voltage drops to several hundred volts due to the high impedance of the transformer, and the discharge stabilizes. The discharge was operated in a millisecond pulsed-dc regime at a constant rms value of 100 mA.

The measured voltage in Fig. 2 includes not only the drop in the gas gap but also the drop in the equivalent resistance of the water electrode. At 0 min, the V–I characteristic curve has a positive slope, reaching a maximum voltage value of about 2 kV, while at 30 min, the slope becomes negative and the voltage drops to about 1.2 kV. This is expected because as the exposure time increases, the conductivity of the water increases (due to the formation of ions in the liquid), and therefore, the resistive voltage drop in the water becomes small compared to that of the gas. The discharge operating power was then calculated from the voltage and current signals at t = 30 min. The resulting power was ≈100 W.

The found voltage (of about 1.2 kV) for the ≈10 mm gas gap is consistent with the cathode voltage drop measurements (600–900 V) reported in the literature for similar discharges [15]. (An axial electric field of 20–40 V/mm can be expected in the positive column under the conditions considered [16]). As a whole, the V–I characteristic curve together with the emissive structure of the discharge (inset of Fig. 1) suggests that the studied discharge has many properties in common with the atmospheric pressure glow-type discharge between two metal electrodes [17] (e.g., the review [5] and references therein). This type of water-cathode discharge is most often referred to as a glow (-like) discharge, but also sometimes as an arc discharge [15]. Moreover, the negative V–I characteristic after 30 min of water activation (t =30 min) (Fig. 2) suggests that for high currents, the predominant ionization mechanism corresponds to associative ionization involving nitrogen and oxygen atoms, which is independent of the reduced electric field. In this sense, the high-temperature values reported by other authors in the gas (≈2000–4000 K) [15] are in agreement with the hypothesis that charge reproduction occurs mainly by associative ionization in atomic collisions (rather than by electron-impact ionization), thus explaining the negative V–I characteristic [16], [18].

No noticeable damage was observed on the metal electrode after several experiments (the electrode erosion is negligible under the experimental conditions considered, and no electrode material—metal vapor—is introduced into the discharge).

III. Treatments and Physicochemical Determinations

Two treatments were used during the experiments.

1) Covering the container with a glass cap during the activation process (closed reactor). Confined air volume ≈330 mL.

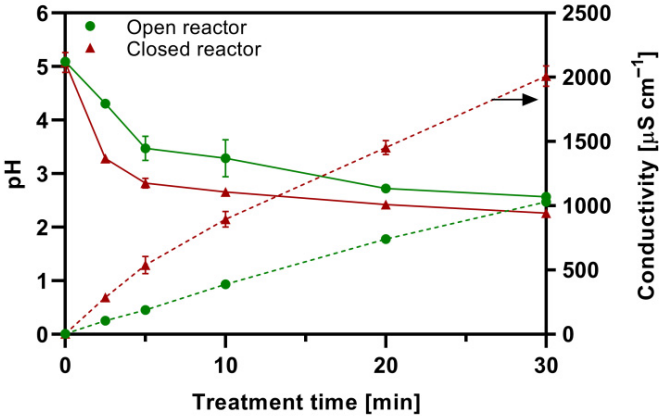

Fig. 3. pH and electrical conductivity of PAW as a function of treatment time (min).

2) Without covering the container (open reactor).

The substantial difference between the two treatments resides in the availability of fresh air: when the glass cap is placed on the container, a closed gas chamber is formed where the discharge is established, and the air molecules are consumed, resulting in the formation of different RONS.

A pH meter (Hanna HI 8314) and a conductivity meter (Oakton Cyberscan Cond 610), previously calibrated, were used to measure the pH and electrical conductivity, respectively, while the protocols established in the standard methods for the examination of water and wastewater [19] were followed to measure the concentrations of NO_3^-, NO_2^-, and H_2O_2 in the aqueous phase. Briefly, H_2O_2 concentration was measured using a peroxidase, which catalyzed the reaction of H_2O_2 with 4-aminophenazone and phenol giving a red product (measured at 505 nm). The UV method (absorbances at 220 and 275 nm) was used for NO_3^- measurements and NO_2^- concentrations were quantified following the Griess technique. Measurements were done with a spectrophotometer UV-VIS Spectrum SP-2100.

Measurements were done in triplicate for each time studied (2.5, 5, 10, 20, and 30 min). PAW stability in the postdischarge phase was followed for 90 days. PAW samples were stored at 4 °C in amber flasks, tightly capped, and in the dark. Data are shown as mean value ± standard error of the mean (SEM). The distilled water from which the PAW was generated had a pH ≈ 5 and a conductivity ≤5 μS/cm.

IV. Results

Fig. 3 shows that pH decreases and electrical conductivity increases with plasma exposure time (treatment time).

The pH reached values of 2.3 and 2.6 at 30 min, for closed and open reactors, respectively, while the electrical conductivity increased approximately linearly with time for both treatments, although with a large difference between their values after the treatment. For the closed reactor, a conductivity value of ≈2000 μS/cm was reached, while for the open reactor, it was ≈1000 μS/cm. The decrease in pH and the increase in conductivity are related to the formation of acids (HNO_2 and HNO_3) and ions (mainly H^+ and

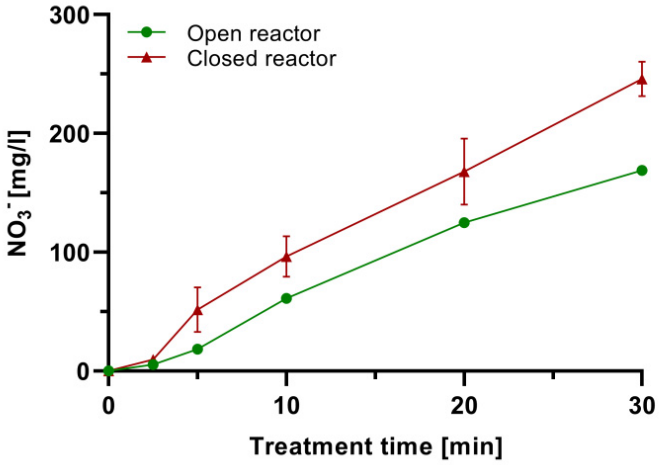

Fig. 4. NO_3^- concentration as a function of treatment time (min).

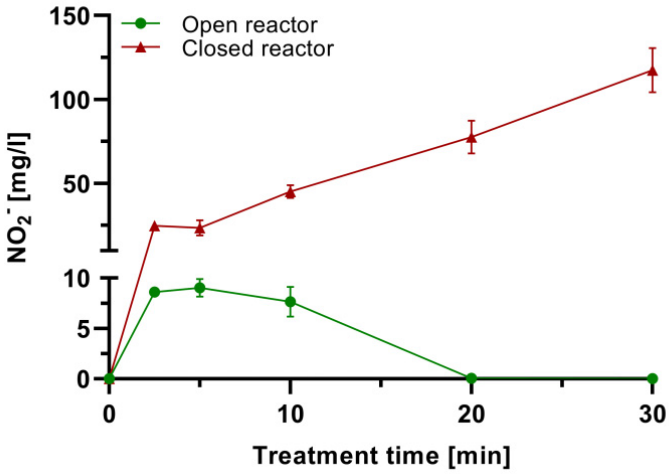

Fig. 5. NO_2^- concentration as a function of treatment time (min).

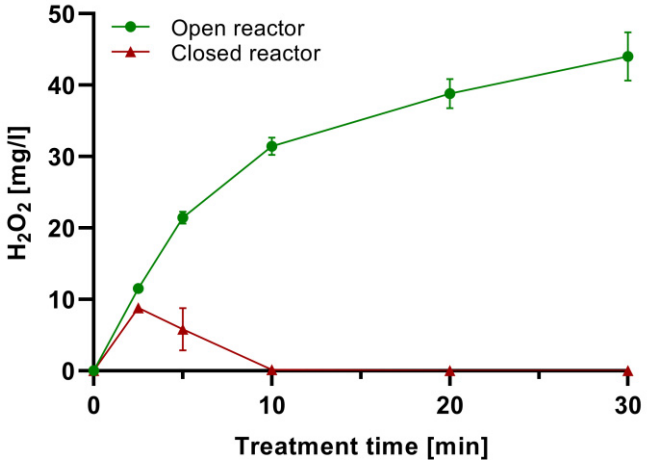

Fig. 6. H_2O_2 concentration as a function of activation time (min).

NO_3^-) in the liquid volume and are characteristic in water in contact with nonthermal discharges in air and similar mixtures [20].

Fig. 4 shows the concentration of NO_3^- in the aqueous phase, and it is evident that for both treatments, it grows approximately linearly with time. The maximum values reached at 30 min were ≈250 mg/L for the closed reactor and ≈170 mg/L for the open reactor. These high values of NO_3^- show the potential of activated water for use as fertilizer [21].

DC-excited discharges in a pin-to-water electrode geometry operating in air at rms current values of 100 mA and a power of 100 W (see the inset of Fig. 1) typically exhibit gas temperatures exceeding 3000 K, electron temperatures of ≈1 eV, and small ionization degrees ($\sim 10^{-5}$) [6]. Under such high gas temperatures and low ionization plasma conditions, the atomic species N and O are produced mainly in the hottest parts of the discharge by collisions among heavy species ($O_2 + M \rightarrow O + O + M$; $N_2 + M \rightarrow N + N + M$, being M a third body), rather than by electron-impact dissociation (e.g., [17], [18]). These, in turn, combine to form NO (via the Zeldovich mechanism [1]) and NO_2, which could then enter from the gas phase to the liquid by diffusion and react with water molecules to form NO_3^- (and also NO_2^-) in the liquid. However, even with much lower concentration in gas phase than NO and NO_2, the gaseous HNO_2 may also play a relevant role in the formation of NO_2^- in the aqueous phase since its Henry's coefficient is four and five orders of magnitude larger than that of NO_2 and NO, respectively [22].

Fig. 5 shows that the concentration of NO_2^- presents very different behaviors between treatments: while in the closed reactor, it grows monotonically, in the open reactor, it grows during the first 2.5 min to a maximum value and then decreases until it is extinguished. For the closed reactor, the maximum value was 120 mg/L at 30 min of treatment, while in the open reactor treatment, it reaches a peak value of ≈7 mg/L at 2.5 min and disappears at 20 min.

Fig. 6 shows the concentration of H_2O_2 as a function of treatment time. A behavior similar to that of nitrite, but inverse with respect to the treatments, is observed. For the open reactor, the concentration increases monotonically, reaching ≈40 mg/L at 30 min, while in the closed reactor, a maximum ≈10 mg/L is reached at 2.5 min and then decays to extinction for times greater than 10 min.

The chemistry in the aqueous phase is strongly related to the transient RONS chemistry in the gas phase, which in turn depends on the operating conditions of the reactor. The NO_2^- and H_2O_2 species react with each other to form peroxynitrous acid (ONOOH), the rate of this reaction being strongly dependent on the pH, occurring at much higher rates the lower the pH [23], [24]

$$NO_2^- + H_2O_2 + H^+ \rightarrow NO_3^- + H_2O + H^+. \quad (1)$$

The elevated aqueous concentrations of hydrogen peroxide observed in open air reactor conditions suggest that in this configuration, some long-lived RONS (i.e., gas-phase reaction timescales ≪ diffusion timescales), such as NO_2 and HNO_2, which in turn are responsible for the creation of nitrite (and also nitrate) in the liquid phase, do not accumulate in the gas phase due to the diffusion of species into the surrounding

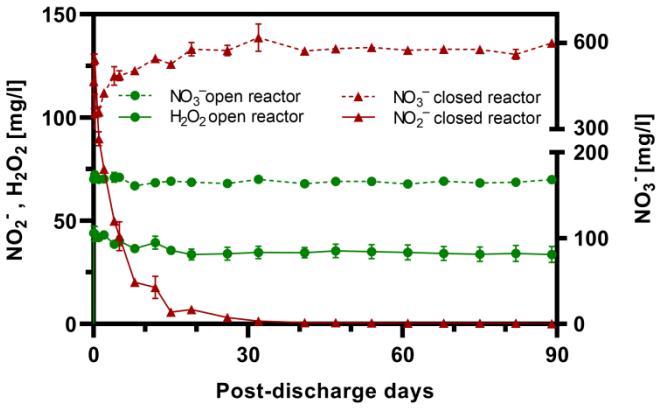

Fig. 7. Concentration of the reactive species in the postdischarge phase for the closed and open reactors.

ambient air. The diffusion timescale ($\equiv d^2/D$, being $d \sim 1$ cm the thickness of the afterglow region and $D \sim 10^{-5}$ m^2/s the diffusion coefficient of species in air at 300 K [1]) is of the order of 1 s under the conditions considered. Therefore, the concentration of NO_2^- in PAW remains low enough (while the pH is not very low) to almost suppress the decomposition of H_2O_2 by nitrites under acidic conditions, according to pathway (1). On the other hand, the higher levels of NO_3^- observed for the closed reactor conditions (Fig. 4) suggest that the air confinement allows the accumulation of such long-lived RONS in the gas phase, which in turn produce a rapid growth in the concentration of NO_2^- (and also a reduction in the pH) with the consequent fast degradation of H_2O_2. It should be noted that the highly reactive hydroxyl radical has gas-phase reaction rates with timescales much shorter than diffusion (i.e., their losses are dominated by gas-phase kinetics rather than diffusion); thus, it is not expected to accumulate, regardless of the mode of operation of the reactor. Note that the combination of dissolved $OH^\cdot$ radicals is likely the main formation pathway of aqueous H_2O_2 in a plasma-liquid system with liquid as cathode [25].

The ONOOH molecule is unstable and degrades faster the lower the pH. It has two paths of destruction

$$O = NOOH \rightarrow OH^\cdot + NO_2^\cdot \quad (2)$$

$$O = NOOH \rightarrow HNO_3 \rightarrow NO_3^- + H^+ \quad (3)$$

and one of them gives as a by-product an $OH^\cdot$ radical. This species is of particular importance in disinfection and decontamination processes because it is highly reactive [7].

In this sense, the mixture of PAW generated in the reactor under open and closed operating conditions becomes an alternative with great potential in disinfection processes, degradation of contaminants, and elimination of bacteria or pathogens due to the availability of $OH^\cdot$ radicals in solution via reaction (2).

Fig. 7 shows the concentrations of the reactive species in the postdischarge phase for both treatments.

For the open reactor, hydrogen peroxide decays slightly in the first 20 days and then remains stable until 90 days, while nitrate remained constant all the period (it is worth mentioning that for this treatment, there is no nitrite immediately after 30 min of exposure). In the closed reactor, where there is no hydrogen peroxide in the postdischarge phase, nitrate increases up to ≈600 mg/L during the first 30 days and then remains stable for 90 days, while nitrite drops rapidly until it disappears after one month. Disappearance in nitrite is to be expected since it is unstable in acidic pH, mostly due to its transformation to nitrate [20]. Tachibana and Nakamura [10] generated four types of PAW: from deionized water and from drinking water, with high and low NO_X^- concentrations ($X = 2$, 3). The authors report that, for low pH, nitrite disappears after several days (between 6 and 40), while for pH close to 7, the concentrations of both species remain stable after 40 days and attribute that nitrite is completely converted to nitrate through several ionic reactions, the following being predominant for storage times of the order of several days:

$$3NO_2^- + 3H^+ \rightarrow 2NO_{aq} + NO_3^- + H_3O^+. \quad (4)$$

V. Conclusion

Physicochemical properties were measured in PAW with a nonthermal glow-type discharge in atmospheric pressure air with a water cathode. The determinations were performed during the activation process and postdischarge (up to 90 days). Two variants (treatments) were used: 1) with the gaseous chamber where the glow discharge is set confined (closed reactor) and 2) with the open chamber (open reactor). The volume treated was 1 L and the maximum exposure time was 30 min. The results are given as follows.

1) The concentration of NO_3^- in the aqueous phase increased with the activation time, reaching maximum concentrations of ≈250 mg/L for the closed reactor and ≈170 mg/L for open reactor.
2) The concentration of NO_2^- in the closed reactor increased with treatment time (≈120 mg/L at 30 min), while in the open reactor, NO_2^- presented a maximum at ≈5 min and then decreased until its extinction at 20 min.
3) H_2O_2 concentration in the open reactor increased with activation time (≈45 mg/L at 30 min), while in the closed reactor, it showed a maximum at 2 and 5 min (≈9 mg/L) and then disappeared for longer times.
4) pH decreased and electrical conductivity increased with activation time for both reactors. The minimum pH values were ≈2 and 2 for closed reactor and ≈2 and 5 for open reactor; while the maximum conductivity values were 2010 μS/cm (closed reactor) and 1030 μS/cm (open reactor).
5) In the postdischarge phase, the concentrations of NO_3^- and H_2O_2 remained practically constant for up to 90 days for the open reactor, while in the closed reactor, NO_2^- concentration decreased markedly until it disappeared at approximately 30 days, while NO_3^- concentration increased simultaneously.

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