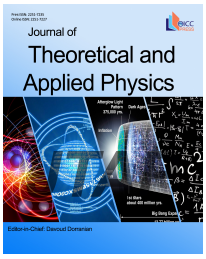

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The effect of cold plasma on the tap water characteristics by changing the liquid electrode conditions

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Abstract:

Analyzing the aqueous system parameters is important for evaluating water quality. This research examined the impact of exerting argon, nitrogen, air, and oxygen cold plasmas on the properties of tap water such as electrical conductivity, pH, and temperature used for various applications at atmospheric pressure. The results demonstrated that electrical conductivity and temperature were ascending-descending in unstirred water and ascending in stirred water at all plasmas. Based on that, stirred water was chosen to investigate pH that showed all plasmas made water acidic. According to pH results in agreement with the previous reports, oxygen gas was chosen with the most decrease in pH to change the acidic result. After filtering the water with argon gas, oxygen plasma caused basic properties in the water. It was found that changing the water (liquid electrode) conditions inside a reactor can produce different results, making it usable in many applications.

Keywords: Electrical conductivity; pH; Plasma; Temperature; Water

1. Introduction

A partially or completely ionized gas is referred to as plasma and is primarily made up of ions, free electrons, photons, molecules, and atoms in the ground or excited states with a net neutral charge. Contrary to neutral gases, plasma is strongly influenced by electric and magnetic fields because of electrically charged particles. Typically, the temperature is used to define plasma quantitatively. Various thermal plasma (TP) and non-thermal plasma (NTP) temperature ranges can be used to describe plasmas. Atoms, molecules, ions, and electrons are not in thermal equilibrium in NTP. So, NTP is sometimes referred to as cold plasma or non-equilibrium plasma. In or extremely close to the equilibrium condition of electrons, ions, and neutrals of plasma often characterize the TP. This wide range of temperature changes enables the use of plasma technologies for a variety of purposes, including air purification, surface sterilization, waste solid material annihilation, surface modification, and surface deposition (coating). Thermal plasmas can't be used at high throughput due to vacuum equipment requirements and non-thermal atmospheric plasma is utilized in this situation. The capacity of NTP to trigger different chemical reactions at ambient pressure and temperature is its most striking characteristic as a chemical process. It is possible to produce cold plasma using a variety of techniques, including corona discharge, ionizing radiation, inductively coupled plasma (ICP), capacitively coupled plasma (CCP), microwave (MW), radio frequency (RF), electron cyclotron resonance (ECR), and dielectric barrier discharge (DBD) plasmas, depending on the applications needed in the industry [1–11].

One of the most important and often performed tests in water chemistry is pH testing. The pH or hydrogen ion activity of a solution at a given temperature indicates whether it is basic (alkaline) or acidic. The pH scale, which spans from 0 to 14 ($pH = 7$ neutral, $pH < 7$ acidic, $pH > 7$ alkaline), measures the acidity or alkalinity of water. Actually, the pH scale measures the proportion of free hydrogen and hydroxide ions in water. The pH is a key factor in every step of the water supply and wastewater treatment processes; including acid-base neutralization, water disinfection, desalination, and corrosion control [12].

Another crucial factor of water that also affects plasma dis-

charge characteristics and the formation of active species is electrical conductivity (EC), which is often used to calculate the total concentration of ionized water components. This parameter, which is closely connected to the total number of anions (or cations) in the solution and is typically proportionate to the total quantity of dissolved solids, is presented as a measure of an aqueous solution's capacity to transfer electric current. Water conductivity often doesn't change over time. As a result, any alteration in conductivity may be a sign of potential water pollution brought on by chemical interactions with water. That determination is quick and somewhat accurate and does not affect the samples. Mineral solution solids have an impact on the electrical conductivity of water. The EC of water can also be impacted by temperature (T) [13].

It could be produced a stable glow discharge at atmospheric pressure using liquid as a cathode or anode. This discharge system is known as electrolysis with a plasma electrode too, focusing on a liquid-phase reaction. The discharge is generated in a gap between a metal electrode and a liquid electrode. The liquid or plasma electrode will transmit electrons and positive ions to the liquid surface in a different way from the common metal electrode. DC glow discharge with the liquid electrode is a plain technique to create a simple and stable plasma-liquid interface [14]. Cold atmospheric pressure plasmas in contact with liquid are widely studied aiming kind of plasma applications [15–17].

More study is required to optimize the discharge circumstances in the creation of the desired chemical species and alter the characteristics of the solutions since the physics and chemistry of various discharge types in aqueous solutions are not yet fully understood. In this study, variations in pH, EC ($\mu S/cm$), and T (°C) parameters for argon, nitrogen, oxygen, and air gases were examined and compared over a short time (4 min, with 0.5 min periods). In the following, the oxygen gas with the most decrease in pH was chosen to change the result by the filtering method. The results showed that a plasma production reactor can be used to produce water with acidic or alkaline characteristics depending on the type of application with a change in the experiment process.

2. Experimental details

Figure 1 displays experimental setup of the glow discharge. In this arrangement, a pyrex container was filled with 250 mL of tap water. Two tungsten electrodes with a 2 mm diameter were used. The anode electrode was placed in the water. The cathode electrode was set within a pyrex tube that was located inside a ceramic tube so that it was 1 cm of the outside of the glass and inside of the ceramic. The water was free of nitrogen and contained oxygen. The feed gas emerged through the end of the pyrex tube with a flow rate of 50 sccm. The gas flow covered the entire area around the cathode to the water surface. Water vapor and feed gas were ionized by applying a large potential difference (8 kV) by a DC power source in the area between the cathode tip and the end of the ceramic tube and entered inside the water. The gas temperature was 300 K [6]. The average plasma electron temperature and density were about 1 eV and 2.5×10^{15} cm^{-3} via the Boltzmann plot and the Stark broadening of the hydrogen Balmer H_β spectral line method [6]. There were two types of water throughout the experiment: unstirred water without a magnetic stirrer (M1) and stirred water with a magnetic stirrer (M2). The electrical discharge of argon, nitrogen, oxygen, and air in water was repeated at 0.5 min periods for 4 min. Water filtering in the case of oxygen discharge to produce water with alkaline properties was carried out in the form of passing argon inside the water for 2 min at 40 °C. Water was cooled to room temperature for test. Water pH and T were measured by desktop pH and T meter (HI2002 - edge® Dedicated pH/T Meter, numerical precision of 0.01 and 0.1, respectively) of HANNA company. Electrical conductivity was measured by Sper scientific, waterproof conductivity meter (pen style,

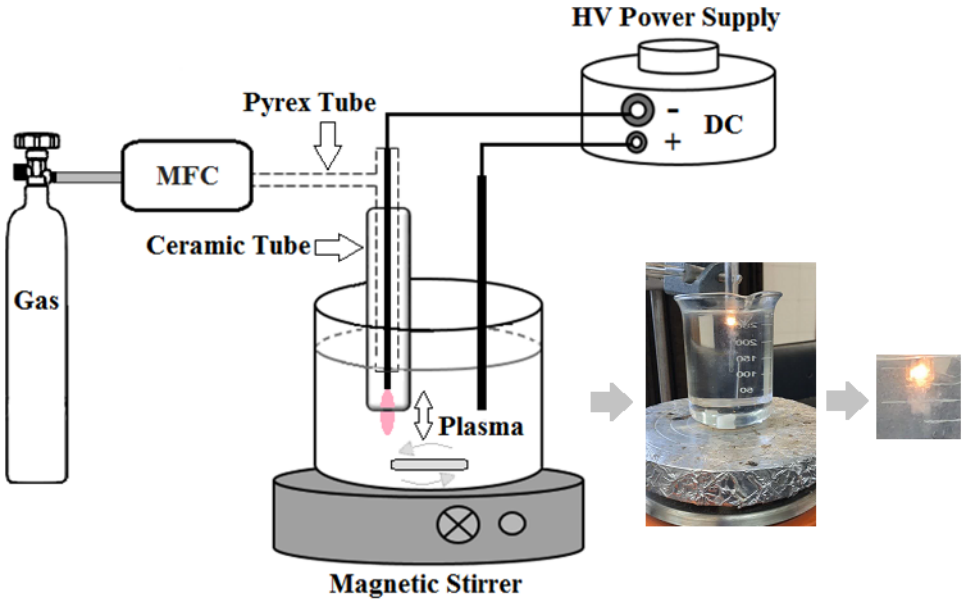

Figure 1. DC glow discharge setup.

numerical precision 1), of Sper Scientific Ltd. Each experiment was repeated five times. The reported values (EC, T, pH, and hydrogen and hydroxide ions concentration) were the average values of five repetitions in each type of plasma at a certain plasma-exerting time.

3. Result and discussion

3.1 Investigation of electrical conductivity and temperature

Active species and ions created during plasma exerting were dissolved in water and changed the EC of the water. Electrical conductivity and temperature changes due to plasma exerting four gases were measured for M1 and M2 waters. Figures 2 and 3 show electrical conductivity and temperature during time change for M1 water. Figures 4 and 5 are for M2 water data. The 0 min is the time before plasma exerting in all plots. As shown in figure 2, electrical conductivity in all plasmas and times was more than before plasma exerting, and the process of its change was ascending and descending at different periods. Fluctuation in conductivity values was caused by M1 of water. The increase in electrical conductivity was caused by entering nitrogen oxide and hydrogen oxide byproducts into the water due to ionizing ambient air, water vapor, and feed gas [18]. It appears that the increasing concentration of reactive ions in water has reduced the electrical conductivity of water in a short amount of time. In other words, making the water more electrically conductive, the diffusion layer near the electrodes with a concentration differing from its value in the volume of water has reached saturation and blocked the entrance of more ions into the water. The escape of ions as reaction products from the diffusion layer in water under the effect of the electric field and chemical potential gradient owing to the difference in concentration, or the consumption of ions, has disrupted the saturation state [19]. This process has been repeated several times for EC.

According to figure 3, the temperature changes were ascending with a slight fluctuation in some cases at various periods and also higher than before plasma exerting. The temperature decreasing in sometimes compared to the previous time was due to the M1 of water.

For all plasmas, percentages of temperature and electrical conductivity variations in M1 water in each period have been compared to before plasma in Table 1.

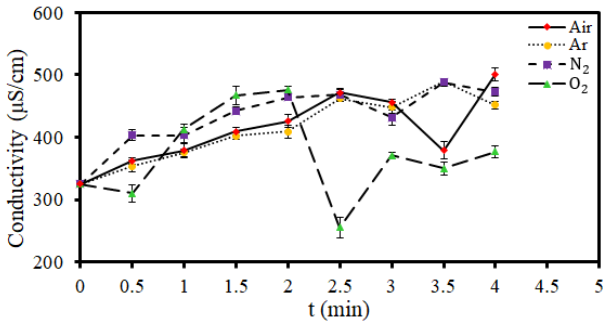

Figure 2. Electrical conductivity changes of M1 water after argon, nitrogen, oxygen, and air plasmas exerting during 4 min.

As shown in figures 4 and 5, EC and T changes in M2 water were increasing at all periods and plasmas in comparison to the prior periods and before plasma exerting.

Stirring and lack of saturation in the water diffusion layer were the causes. Electrical conductivity has altered with temperature variations in all plasmas. Increasing the temperature of the water has also raised the ions' mobility and the number of ions due to the separation of molecules in water.

For all plasmas, percentages of temperature and electrical conductivity variations in M2 water in each period have been compared to before plasma in Table 2. Plasma-

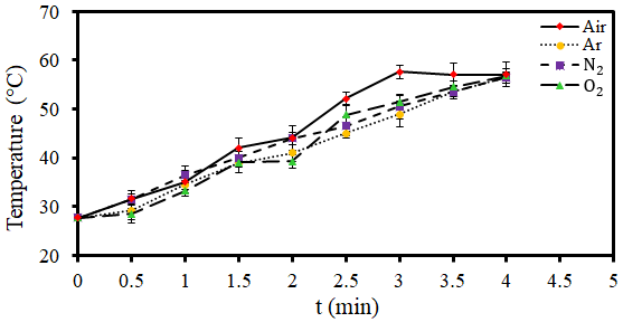

Figure 3. Temperature changes of M1 water after argon, nitrogen, oxygen, and air plasmas exerting during 4 min.

Table 1. Percentages of temperature and electrical conductivity variations in M1 water in each period compared to before argon, nitrogen, air, and oxygen plasma.

Δ(t) (min)	$\Delta(T)_{Ar}$ (%)	$\Delta(EC)_{Ar}$ (%)	$\Delta(T)_{N_2}$ (%)	$\Delta(EC)_{N_2}$ (%)	$\Delta(T)_{O_2}$ (%)	$\Delta(EC)_{O_2}$ (%)	$\Delta(T)_{Air}$ (%)	$\Delta(EC)_{Air}$ (%)
0.5	5.42	8.92	13.72	24	2.89	11.08	14.08	11.38
1	24.55	15.38	31.77	24	20.22	20.62	26.71	16.62
1.5	40.79	23.69	44.40	36	41.16	18.15	51.99	25.84
2	48.01	25.85	58.84	42.77	41.88	20.62	59.21	31.08
2.5	62.45	42.15	67.87	44	76.17	13.85	88.09	45.23
3	21.3	37.85	82.31	32.62	85.92	19.69	107.94	40.31
3.5	93.14	50.46	93.14	50.15	97.11	11.08	106.14	16.62
4	103.97	39.08	103.97	45.54	105.05	7.08	106.14	54.15

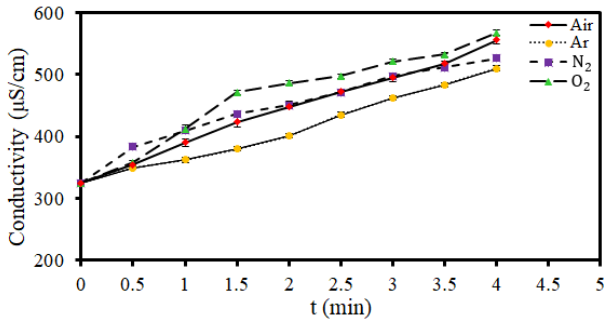

Figure 4. Electrical conductivity changes of M2 water after argon, nitrogen, oxygen, and air plasmas exerting during 4 min.

activated water (PAW) generated by cold atmospheric plasma (CAP)-water interaction employing controllable parameters has been reported to have higher conductivity [20]. According to the results of the significant increase in conductivity for M2 water, and its high rise in PAW reported in several study cases, M2 water was selected for further investigation.

3.2 Investigation of pH and concentration of hydrogen and hydroxide ions

Although measuring and analyzing pH levels is one of the major metrics to certify the standards of the water industry, it can play a fundamental role across a wide range of industries including the food industry and agriculture. The pH standing for the power of hydrogen describes the concentration of hydrogen ions in a solution. Figures 6 to 9 display the pH, hydrogen cation, and hydroxide anion concentration variations of M2 water for each plasma as a function of time. The concentrations of hydrogen and hydroxide ions have been calculated with formulas $[H^+] = 10^{-pH}$ and $[OH^-] = 10^{-pOH}$ [12]. As can be seen in figure 6 (a) for argon plasma, there was a low rise in the sample's pH after 0.5 min. It decreased in 0.5 – 1.5 min, increased at 2 min, and then decreased at 2.5 min. The pH went up at 3 min and reduced again with a low slope at 4 min. However, the water was acidic during the whole experiment. Figure 6 (b) shows that the concentration of hydrogen cation was always more than hydroxide anion in argon plasma.

According to figure 7, the water had higher concentrations of hydrogen cations than hydroxide anion and was acidic due to the exerting of nitrogen gas plasma. After plasma exerting for 0.5 min, a rise in pH was seen. It went down

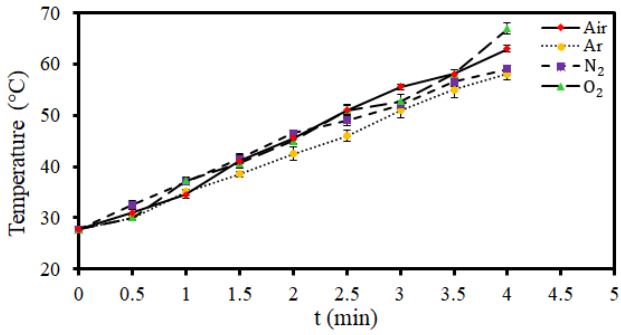

Figure 5. Temperature changes of M2 water after argon, nitrogen, oxygen, and air plasmas exerting during 4 min.

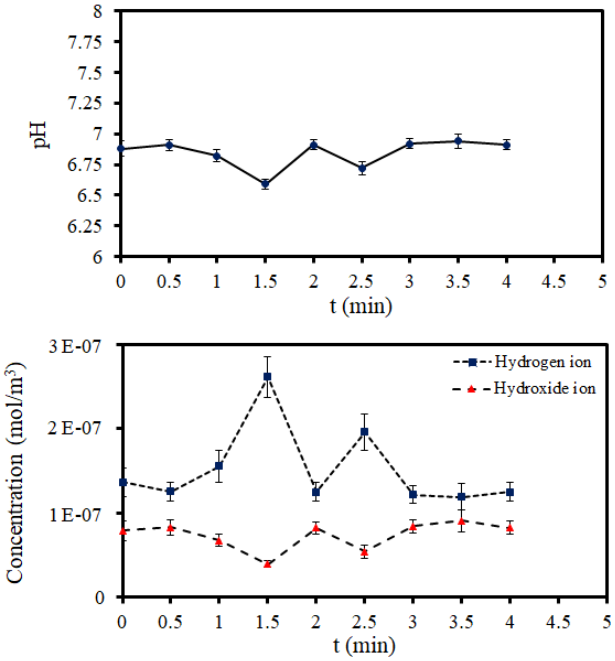

Figure 6. Changes of (a) pH and (b) hydrogen and hydroxide ions concentrations of M2 water in argon plasma.

Table 2. Percentages of temperature and electrical conductivity variations in M2 water in each period compared to before argon, nitrogen, air, and oxygen plasma.

Δ(t) (min)	$\Delta(T)_{Ar}$ (%)	$\Delta(EC)_{Ar}$ (%)	$\Delta(T)_{N_2}$ (%)	$\Delta(EC)_{N_2}$ (%)	$\Delta(T)_{O_2}$ (%)	$\Delta(EC)_{O_2}$ (%)	$\Delta(T)_{Air}$ (%)	$\Delta(EC)_{Air}$ (%)
0.5	8.30	7.38	17.33	17.85	8.30	7.38	11.91	8.92
1	26.35	11.38	33.57	25.85	34.30	17.54	24.55	20
1.5	38.99	16.92	49.82	34.15	46.57	23.69	48.01	30.15
2	53.43	23.38	67.87	38.46	62.45	30.77	64.26	37.85
2.5	66.06	33.84	76.90	44.92	84.12	40.62	84.12	45.23
3	84.12	42.15	87.73	52.92	90.25	51.08	100.36	52.31
3.5	98.56	48.62	103.97	57.23	109.39	61.23	109.39	59.08
4	109.39	56.92	113.00	61.85	141.52	80.62	127.44	71.08

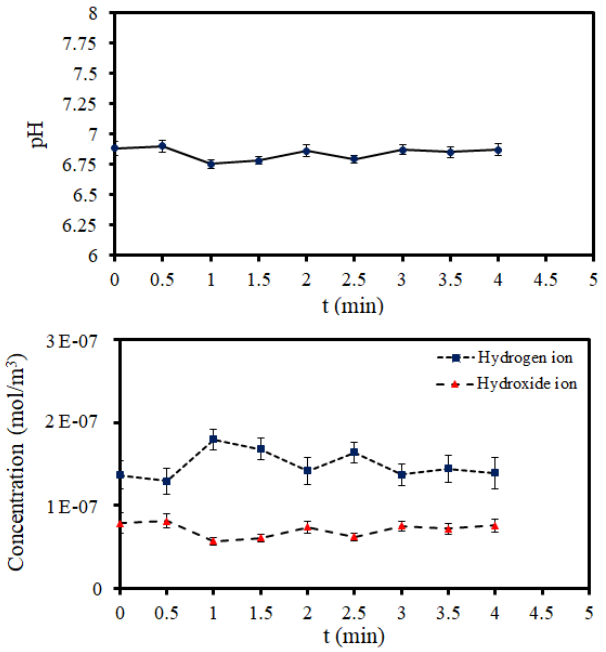

Figure 7. Changes of (a) pH and (b) hydrogen and hydroxide ions concentrations of M2 water in nitrogen plasma.

at 1 min and went up at 2 min. It decreased at 2.5 min. After increasing at 3 min, there was a decline at 3.5 min and ultimately rise at 4 min.

In figure 8, air plasma has increased the concentration of hydrogen cation relative to hydroxide anion and acidified the water. The 0.5 min of electric discharge resulted in a pH drop. The changes trend was upward in $0.5-2$ min and downward in $2-3$ min. It rose at 3.5 min and then fell at 4 min.

The results of oxygen plasma on the pH and concentrations of hydrogen cations and hydroxide anions are shown in figure 9. It has made the water acidic. The $0-1.5$ min of electric discharge resulted in a pH decrease. The pH increased at 2 min. The changes trend was downward in $2.5-3$ min and upward at 3.5 min. It reduced at 4 min.

The prior stated results of this study were in agreement with the acidic values pH of PAW generated by CAP in previous reports [21–25]. So, an attempt was made to create a possibility to increase the water pH with the same setup instead of decreasing it. The tap water was filtered with inert argon gas before exerting the plasma to remove other gases inside the water. Oxygen gas, which caused the most acidic property in water, was selected for plasma production.

The results of oxygen plasma after filtering are shown in figure 10. As can be seen in figure 10 (a), pH increased after 0.5 min of electric discharge and subsequently decreased at 1 min. The pH enhanced at 1.5 min, reduced at $2-2.5$ min, then climbed again in $3-3.5$ min and finally went down at 4 min. According to figure 10 (b), water had more hydroxide anion than hydrogen cation in the whole experiment, indicating that oxygen plasma behaved differently from before. The composition and reaction of the active species in oxygen plasma led to basic water after clearing. As shown in figures 10 (c) and (d), EC and T changes at all periods obtained more than the prior periods and before plasma exerting. For oxygen plasmas, percentages of temperature and electrical conductivity variations after filtering in each period have been compared to before plasma in Table 3.

As illustrated in figure 11, the plasma exerting resulted in the generation of reactive oxygen species (ROS), reactive nitrogen species (RNS), and reactive hydrogen species (RHS) in the water due to direct interactions and several indirect cascade phenomena including liquid evaporation, molecules collision, mass transfer, sputtering, and ultra-violet radia-

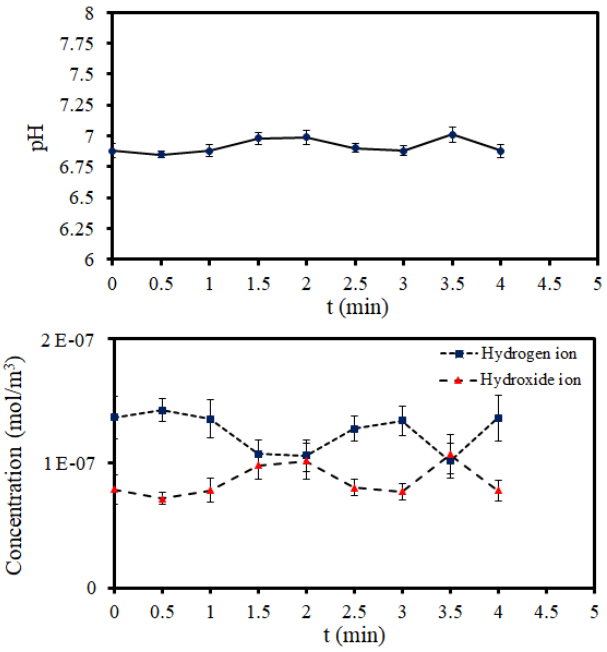

Figure 8. Changes of (a) pH and (b) hydrogen and hydroxide ions concentrations of M2 water in air plasma.

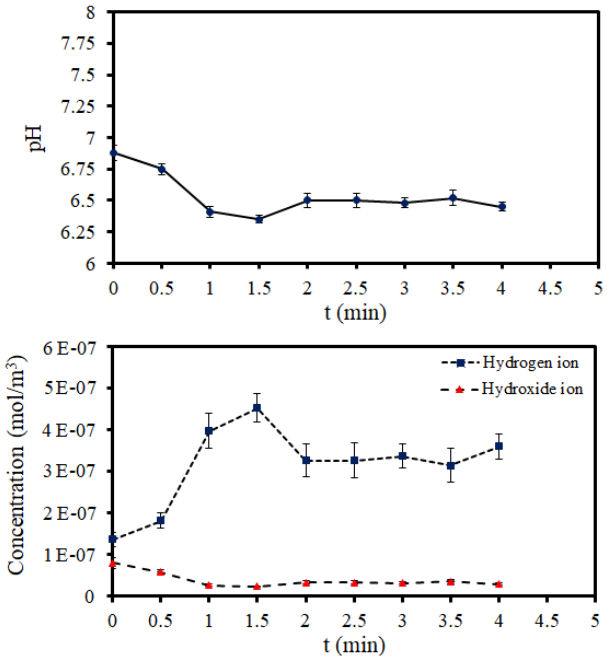

Figure 9. Changes of (a) pH and (b) hydrogen and hydroxide ions concentrations of M2 water in oxygen plasma.

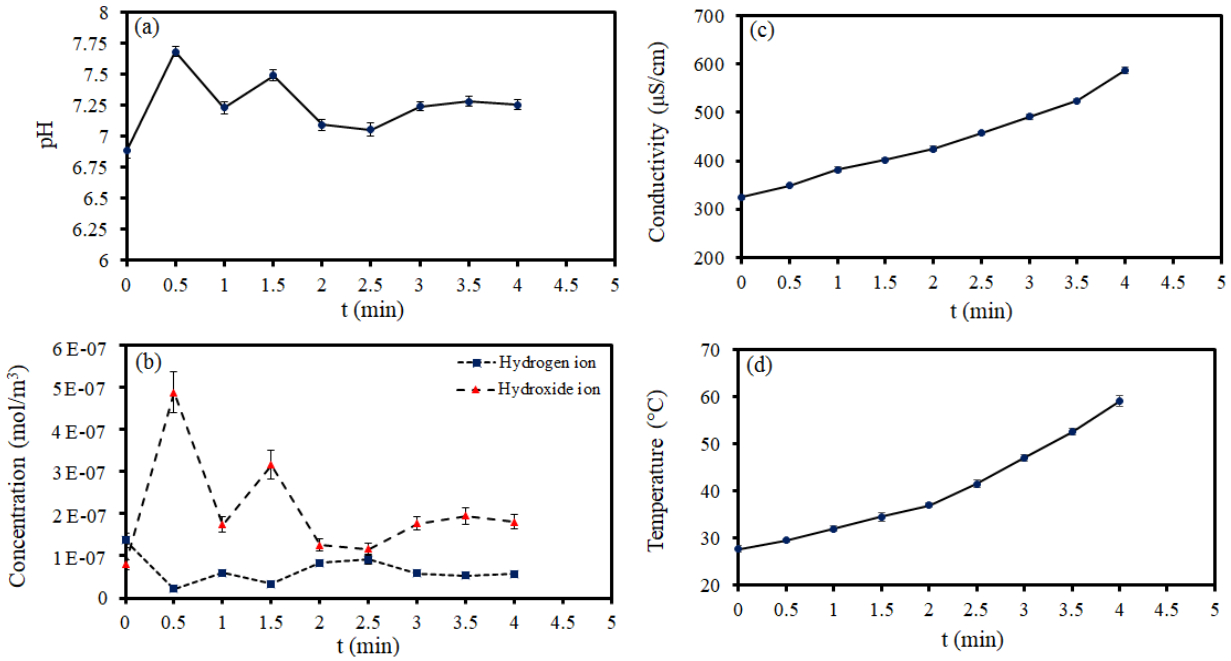

Figure 10. Changes of (a) pH, (b) hydrogen and hydroxide ions concentrations, (c) Electrical conductivity, and (d) Temperature of M2 water in oxygen plasma after filtering.

tion at the plasma phase, plasma-water interface, and liquid phase [26].

Table 4 displays the more probable reactions over (between electrode tip and the water surface) and inside the water that resulted in acidic and basic characteristics of tap water. Producer reactions of reactants leading to acidic or basic properties were also determined. (Ar), (N_2), (O_2) and (Air) symbols denoted the usual reactions of argon, nitrogen, and air plasma. (O_2:A) and (O_2:B) symbols show oxygen plasma reactions lead to acidic and basic characteristics. Before filtering, the reactive oxygen-nitrogen species (RNOS) were generated by argon, nitrogen, air, and oxygen plasmas interacting with water and water vapor. The hydrogen cations (H^+) making acidic qualities in water were dominated in Ar, N, (O_2:A) and, Air plasmas and were created by the interaction of RNOS with hydrogen and oxygen species in water. The most acidic water created by oxygen plasma was selected. After filtering, the hydroxide anions (OH^-) producer reactions were dominated and made water basic. The hydrogen and oxygen species were the most precursor of OH^- in the plasma-water interaction. In all plasmas, hydrogen gas around the cathode and oxygen gas in the vicinity of the anode was produced [6, 44, 45].

This research showed that in using the capacity of CAP, a small variation in reactor design can make a different property in water under plasma exerting depending on the application type compared to the state before. Here, water filtering with argon gas before exerting oxygen plasma made water basic instead of acidic which is different from previous reports [46]. According to these characteristics,

Table 3. Percentages of temperature and electrical conductivity variations in M2 water in each period after filtering compared to before oxygen plasma.

Δ(t) (min)	$\Delta(T)_{O_2}$ (%)	$\Delta(EC)_{O_2}$ (%)
0.5	5.42	10.15
1	15.52	26.77
1.5	24.55	44.92
2	33.57	49.54
2.5	49.82	52.92
3	69.68	60.30
3.5	89.53	63.69
4	113.00	74.46

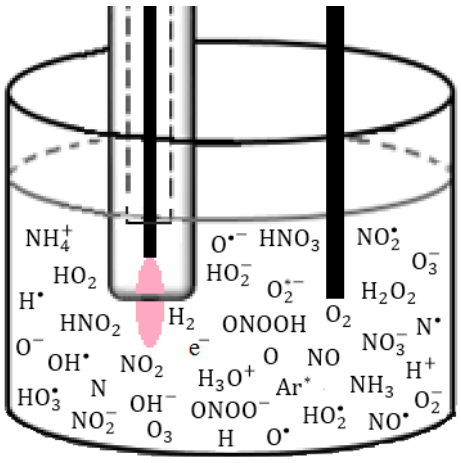

Figure 11. Schematic representation of reactive oxygen species (ROS), reactive nitrogen species (RNS), and reactive hydrogen species (RHS) resulting from the dominant reactions of argon, nitrogen, oxygen, and air plasmas in water.

cold plasma can be introduced as an emerging technology compatible with the environment, which can have a unique position in modern applications required by societies, including improving agricultural methods and food industries (increasing shelf life and quality characteristics of fresh products, seed germination, and plant growth), health and medical usages (anti-infection of medical equipment, treatment of skin, digestive, and cancer diseases), and water industry (urban and industrial water and wastewater treatment, electrolysis, and hydrogen fuel) by forming RHS, RNS, and ROS, and changing electrical conductivity and the chemical composition of water [6, 47–66].

4. Conclusion

The pH, EC, and T of the water change depending on the kind of reactor and plasma application gas used. In the planned reactor, a noticeable ascending-descending pattern was observed in M1 water in electrical conductivity and temperature variations by plasma exerting during different times. This process was observed ascending in M2 water for conductivity and temperature at all times. Argon, air, nitrogen, and oxygen plasmas made M2 water acidic slightly. It was more in oxygen plasma than the others. Oxygen plasma made M2 water basic after filtering water by argon gas and EC and T changes were ascending like before filtering. According to the announced results, it was possible to create different properties in water with the same reactor design by changing the plasma exerting process. This feature can confer the possibility of a reactor being used in countless applications.

Authors contributions
Mohammad Ali Mohammadi: Supervising and reviewing. Targol Naghibzadeh: Visualization, writing-original draft, resources, and manuscript editing. Fatemeh Baharlounezhad: Visualization, writing-original draft, resources, supervising, reviewing, and manuscript editing. Mohammad Sadegh Zakerhamidi: Supervising and reviewing.

Availability of data and materials
The authors declare that the data supporting the findings of this study are available within the paper.

Conflict of interests
The authors declare no conflict of interest.

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Table 4. The probable reactions over and inside the water leading to acidic and basic properties in each of the plasmas [27–43].

Ar^*	
$Ar + e^- \rightarrow Ar^* + e^-$	(Ar)
N	
$O_2^{*-} + N_2 \rightarrow 2N + O_2$	(N_2)
$N_2 + h\nu \rightarrow 2N$	(N_2)
NO	
$N + O \rightarrow NO$	(N_2), (Air)
$N + OH^\bullet \rightarrow NO + H$	(N_2), (Air)
$N + O_2 \rightarrow NO + O$	(N_2), (Air)
$N^\bullet + O^\bullet \rightarrow NO$	(N_2), (Air)
$N + O_3 \rightarrow NO + O_2$	(N_2), (Air)
$N + O_2^\bullet \rightarrow NO + O$	(N_2), (Air)
$3NO_2 + H_2O \rightarrow NO + 2HNO_3$	(N_2), (Air)
$NO_2^- + OH^\bullet \rightarrow NO + HO_2$	(N_2), (Air)
$ONOO^- \rightarrow NO + O_2^{*-}$	(N_2), (Air)
$3NO_2^- + 3H^+ \rightarrow 2NO + NO_3^- + H_3O^+$	(N_2), (Air)
$2NO_2^- + 2H^+ \rightarrow NO + NO_2 + H_2O$	(N_2), (Air)
NO_2	
$O^\bullet + NO \rightarrow NO_2$	(N_2), (Air)
$2NO_2^- + 2H^+ \rightarrow NO + NO_2 + H_2O$	(N_2), (Air)
$O_2^{*-} + N \rightarrow NO_2$	(N_2), (Air)
$NO + O_3 \rightarrow NO_2 + O_2$	(N_2), (Air)
$2NO + O_2 \rightarrow 2NO_2$	(N_2), (Air)
$NO^\bullet + HO_2^\bullet \rightarrow NO_2 + OH$	(N_2), (Air)
$N^\bullet$	
$N_2 + e^- \rightarrow 2N^\bullet + e^-$	(N_2), (Air)
$2N_2 + O_2^- \rightarrow 2N^\bullet + 2NO^\bullet$	(N_2), (Air)
$NO^\bullet$	
$2HNO_2 \rightarrow NO^\bullet + NO_2^\bullet + H_2O$	(N_2), (Air)
$2N_2 + O_2^- \rightarrow 2NO^\bullet + 2N^\bullet$	(N_2), (Air)
$NO_2^- + h\nu \rightarrow NO^\bullet + O^{\bullet-}$	(N_2), (Air)
$3NO_2^- + 2H^+ \rightarrow NO_3^- + 2NO^\bullet + H_2O$	(N_2), (Air)
$NO_2^\bullet$	
$2HNO_2 \rightarrow NO^\bullet + NO_2^\bullet + H_2O$	(N_2), (Air)
$NO_3^- + h\nu \rightarrow NO_2^\bullet + O^{\bullet-}$	(N_2), (Air)
NO_2^-	
$NO + H_2 \rightarrow 2H^+ + NO_2^- + e^-$	(N_2), (Air)
$4NO + O_2 + 2H_2O \rightarrow 4NO_2^- + 4H^+$	(N_2), (Air)
$2NO_2 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+$	(N_2), (Air)
$NO + NO_2 + H_2O \rightarrow 2NO_2^- + 2H^+$	(N_2), (Air)
$HO_2 + NO_2 \rightarrow NO_2^- + O_2 + H^+$	(N_2), (Air)
$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O$	(N_2), (Air)
$4NO^\bullet + O_2 + 2H_2O \rightarrow 4NO_2^- + 4H^+$	(N_2), (Air)

Continue of Table 4

$3NO_2^{\bullet} + H_2O_2 \rightarrow NO_2^- + 2NO_3^- + 2H^+$	(N_2), (Air)
$NO_3^- + h\nu \rightarrow NO_2^- + O$	(N_2), (Air)
NO_3^-	
$3NO_2^- + 3H^+ \rightarrow NO_3^- + 2NO + H_3O^+$	(N_2), (Air)
$2NO_2 + H_2O \rightarrow NO_3^- + NO_2^- + 2H^+$	(N_2), (Air)
$NO_2 + OH^{\bullet} \rightarrow NO_3^- + H^+$	(N_2), (Air)
$HNO_3 \rightarrow NO_3^- + H^+$	(N_2), (Air)
$ONOOH \rightarrow NO_3^- + H^+$	(N_2), (Air)
$H_2O_2 + NO_2^- + H^+ \rightarrow NO_3^- + H_2O + H^+$	(N_2), (Air)
$NO_2^- + O_3 \rightarrow NO_3^- + O_2$	(N_2), (Air)
$3NO_2^- + 2H^+ \rightarrow NO_3^- + 2NO^{\bullet} + H_2O$	(N_2), (Air)
$4NO_2^{\bullet} + O_2 + 2H_2O \rightarrow 4NO_3^- + 4H^+$	(N_2), (Air)
$3NO_2^{\bullet} + H_2O_2 \rightarrow NO_2^- + 2NO_3^- + 2H^+$	(N_2), (Air)
O	
$O_2 + e^- \rightarrow 2O + e^-$	(Ar), (N_2), (O_2), (Air)
$O_2 + h\nu \rightarrow 2O$	(Ar), (N_2), (O_2), (Air)
$O_2 + e^- \rightarrow O + O^-$	(Ar), (N_2), (O_2), (Air)
$N + O_2 \rightarrow O + NO$	(N_2), (Air)
$N + O_2^{\bullet} \rightarrow O + NO$	(N_2), (Air)
$NO_3^- + h\nu \rightarrow NO_2^- + O$	(N_2), (Air)
$Ar^* + O_2 \rightarrow 2O + Ar$	(Ar)
O_3	
$O + O_2 \rightarrow O_3$	(Ar), (N_2), (O_2), (Air)
$O^{\bullet}$	
$O_2 + e^- \rightarrow 2O^{\bullet} + e^-$	(Ar), (N_2), (O_2), (Air)
O^-	
$O_2 + e^- \rightarrow O^- + O$	(Ar), (N_2), (O_2), (Air)
O_2^-	
$O_2 + H^{\bullet} \rightarrow HO_2^{\bullet -} \leftrightarrow H^+ + O_2^-$	(Ar), (N_2), (O_2:A), (Air)
$O_2 + e^- \rightarrow O_2^-$	(Ar), (N_2), (O_2), (Air)
$2OH^{\bullet} + 2OH^{\bullet} \rightarrow O_2^- + 2H_2O$	(Ar), (N_2), (O_2), (Air)
$O_3 + HO_2^{\bullet} \rightarrow O_2^- + OH^{\bullet} + O_2$	(Ar), (N_2), (O_2), (Air)
$OH + O_3 \rightarrow 2O_2^- + H^+$	(Ar), (N_2), (O_2), (Air)
$OH + O_3 \rightarrow O_2^- + HO_2^{\bullet}$	(Ar), (N_2), (O_2), (Air)
O_3^-	
$O_2^- + O_3 \rightarrow O_3^- + O_2$	(Ar), (N_2), (O_2), (Air)
$HO_2^- + O_3 \rightarrow O_3^- + HO_2$	(Ar), (N_2), (O_2), (Air)
$3OH + O_3 \rightarrow 3H^+ + 2O_3^-$	(Ar), (N_2), (O_2), (Air)
O_2^{*-}	
$ONOO^- \rightarrow NO + O_2^{*-}$	(N_2), (Air)
$O^{\bullet -}$	
$NO_2^- + h\nu \rightarrow NO^{\bullet} + O^{\bullet -}$	(N_2), (Air)
$NO_3^- + h\nu \rightarrow NO_2^{\bullet} + O^{\bullet -}$	(N_2), (Air)

Continue of Table 4

H	
$H_2O + h\nu \rightarrow OH + H$	(Ar), (N_2), (O_2), (Air)
$H_2O + e^- \rightarrow OH + H$	(Ar), (N_2), (O_2), (Air)
$H_2O \rightarrow H + OH$	(Ar), (N_2), (O_2), (Air)
$O_2 + 3H \rightarrow H + 2OH^\bullet$	(Ar), (N_2), (O_2), (Air)
$H_2O + e^- \rightarrow H + OH^\bullet$	(Ar), (N_2), (O_2), (Air)
$N + OH^\bullet \rightarrow H + NO$	(N_2), (Air)
$H^\bullet$	
$H_2O \rightarrow H^\bullet + OH^\bullet$	(Ar), (N_2), (O_2), (Air)
$2H_2O + e^- \rightarrow H_2O_2 + 2H^\bullet + e^-$	(Ar), (N_2), (O_2), (Air)
$H_2O + e^- \rightarrow OH^\bullet + H^\bullet + e^-$	(Ar), (N_2), (O_2), (Air)
$2N + 2H_2O \rightarrow 2H^\bullet + N_2 + 2OH^\bullet$	(N_2), (Air)
$Ar^* + H_2O \rightarrow Ar + H^\bullet + OH^\bullet$	(Ar)
H^+	
$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$	(Ar), (N_2), (O_2:A), (Air)
$O_2 + H^\bullet \rightarrow HO_2^{\bullet -} \rightarrow H^+ + O_2^-$	(Ar), (N_2), (O_2:A), (Air)
$OH + O_3 \rightarrow H^+ + 2O_2^-$	(Ar), (N_2), (O_2), (Air)
$3OH + O_3 \rightarrow 3H^+ + 2O_3^-$	(Ar), (N_2), (O_2), (Air)
$NO + H_2O \rightarrow 2H^+ + NO_2^- + e^-$	(N_2), (Air)
$4NO + O_2 + 2H_2O \rightarrow 4H^+ + 4NO_2^-$	(N_2), (Air)
$2NO_2 + H_2O \rightarrow 2H^+ + NO_2^- + NO_3^-$	(N_2), (Air)
$NO_2 + OH^\bullet \rightarrow H^+ + NO_3^-$	(N_2), (Air)
$NO + NO_2 + H_2O \rightarrow 2H^+ + 2NO_2^-$	(N_2), (Air)
$OH^\bullet + NO_2^\bullet \rightarrow H^+ + ONOO^-$	(N_2), (Air)
$HO_2 + NO_2 \rightarrow H^+ + NO_3^- + O_2$	(N_2), (Air)
$HNO_3 \rightarrow H^+ + NO_3^-$	(N_2), (Air)
$ONOOH \rightarrow H^+ + NO_3^-$	(N_2), (Air)
$H_2O_2 + NO_2^- + H^+ \rightarrow H^+ + NO_3^- + H_2O$	(N_2), (Air)
$4NO^\bullet + O_2 + 2H_2O \rightarrow 4H^+ + 4NO_2^-$	(N_2), (Air)
$4NO_2^\bullet + O_2 + 2H_2O \rightarrow 4H^+ + 4NO_3^-$	(N_2), (Air)
$3NO_2^\bullet + H_2O_2 \rightarrow NO_2^- + 2NO_3^- + 2H^+$	(N_2), (Air)
OH	
$H_2O + h\nu \rightarrow OH + H$	(Ar), (N_2), (O_2), (Air)
$H_2O + e^- \rightarrow OH + H$	(Ar), (N_2), (O_2), (Air)
$H_2O \rightarrow H + OH$	(Ar), (N_2), (O_2), (Air)
$O_3 + H_2O_2 \rightarrow HO_2 + OH + O_2$	(Ar), (N_2), (O_2), (Air)
$O_3 + HO_2 \rightarrow 2O_2 + OH$	(Ar), (N_2), (O_2), (Air)
$NO^\bullet + HO_2^\bullet \rightarrow NO_2 + OH$	(N_2), (Air)
$H_2O_2 + e^- \rightarrow OH^- + OH$	(O_2:B)
$HO_2^-O + H_2O + e^- \rightarrow 2OH^- + OH$	(O_2:B)
$OH^\bullet$	
$HO_3^\bullet \rightarrow OH^\bullet + O_2$	(Ar), (N_2), (O_2:B), (Air)
$O_3 + H_2O \rightarrow 2OH^\bullet + O_2$	(Ar), (N_2), (O_2), (Air)

Continue of Table 4

$O_3 + HO_2^{\bullet} \rightarrow OH^{\bullet} + O_2 + O_2^-$	(Ar), (N_2), (O_2), (Air)
$O_2 + 3H \rightarrow 2OH^{\bullet} + H$	(Ar), (N_2), (O_2), (Air)
$O_3 + HO_2^{\bullet} \rightarrow OH^{\bullet} + 2O_2$	(Ar), (N_2), (O_2), (Air)
$H_2O + O \rightarrow 2OH^{\bullet}$	(Ar), (N_2), (O_2), (Air)
$H_2O \rightarrow H^{\bullet} + OH^{\bullet}$	(Ar), (N_2), (O_2), (Air)
$H_2O + e^- \rightarrow OH^{\bullet} + H^{\bullet} + e^-$	(Ar), (N_2), (O_2), (Air)
$H^{\bullet} + H_2O_2 \rightarrow H_2O + OH^{\bullet}$	(Ar), (N_2), (O_2), (Air)
$H_2O + e^- \rightarrow H + OH^{\bullet}$	(Ar), (N_2), (O_2), (Air)
$O_3 + H_2O_2 \rightarrow OH^{\bullet} + O_2 + HO_2^{\bullet}$	(Ar), (N_2), (O_2), (Air)
$2H_2O \rightarrow H_3O^+ + OH^{\bullet} + e^-$	(Ar), (N_2), (O_2), (Air)
$2N + 2H_2O \rightarrow N_2 + 2H^{\bullet} + 2OH^{\bullet}$	(N_2), (Air)
$H_2O_2 + e^- \rightarrow OH^{\bullet} + OH^-$	(O_2:B)
$O^{\bullet -} + H_2O \rightarrow OH^{\bullet} + OH^-$	(O_2:B)
$Ar^* + H_2O \rightarrow Ar + H^{\bullet} + OH^{\bullet}$	(Ar)
OH^-	
$H_2O_2 + e^- \rightarrow OH^- + OH^{\bullet}$	(O_2:B)
$OH^{\bullet} + e^- \rightarrow OH^-$	(O_2:B)
$H_2O_2 + e^- \rightarrow OH^- + OH$	(O_2:B)
$OH + e^- \rightarrow OH^-$	(O_2:B)
$2O^- + e^- + H_2 \rightarrow 2OH^-$	(O_2:B)
$OH^{\bullet} + e^- \rightarrow OH^-$	(O_2:B)
$HO_2^- + H_2O + e^- \rightarrow 2OH^- + OH$	(O_2:B)
$H_2O + H + e^- \rightarrow OH^- + H_2$	(O_2:B)
$HO_2^{\bullet} + H_2O_2 \rightarrow OH^- + O_2 + H_2O$	(O_2:B)
$2H_2O + 2e^- \rightarrow 2OH^- + H_2$	(O_2:B)
$O_3 + H_2O + 2e^- \rightarrow 2OH^- + O_2$	(O_2:B)
$O^{\bullet -} + H_2O \rightarrow OH^{\bullet} + OH^-$	(O_2:B)
HO_2	
$OH^{\bullet} + H_2O_2 \rightarrow HO_2 + H_2O$	(Ar), (N_2), (O_2), (Air)
$OH + O_3 \rightarrow HO_2 + O_2$	(Ar), (N_2), (O_2), (Air)
$O_3 + H_2O_2 \rightarrow HO_2 + OH + O_2$	(Ar), (N_2), (O_2), (Air)
$HO_2^- + O_3 \rightarrow HO_2 + O_3^-$	(Ar), (N_2), (O_2), (Air)
$H + O_2 \rightarrow HO_2$	(Ar), (N_2), (O_2), (Air)
$NO_2^- + OH^{\bullet} \rightarrow HO_2 + NO$	(N_2), (Air)
$HO_2^{\bullet}$	
$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}$	(Ar), (N_2), (O_2), (Air)
$O_3 + H_2O_2 \rightarrow OH^{\bullet} + O_2 + HO_2^{\bullet}$	(Ar), (N_2), (O_2), (Air)
$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet}$	(Ar), (N_2), (O_2), (Air)
$OH + O_3 \rightarrow HO_2^{\bullet} + O_2^-$	(Ar), (N_2), (O_2), (Air)
HO_2^-	
$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$	(Ar), (N_2), (O_2:A), (Air)
$O_3 + OH^- \rightarrow HO_2^- + O_2$	(Ar), (N_2), (O_2:A), (Air)
$H_2O_2 \rightarrow HO_2^- + H_3O^+$	(Ar), (N_2), (O_2), (Air)

Continue of Table 4

$HO_3^{\bullet}$	
$O_3^- + H^+ \rightarrow HO_3^{\bullet}$	(Ar), (N_2), (O_2:B), (Air)
H_3O^+	
$H_2O_2 \rightarrow H_3O^+ + HO_2^-$	(Ar), (N_2), (O_2:A), (Air)
$2H_2O \rightarrow H_3O^+ + OH^{\bullet} + e^-$	(Ar), (N_2), (O_2:A), (Air)
$3NO_2^- + 3H^+ \rightarrow H_3O^+ + 2NO + NO_3^-$	(N_2), (Air)
H_2O_2	
$O^{\bullet} + H_2O \rightarrow H_2O_2$	(Ar), (N_2), (O_2), (Air)
$O_3 + H_2O \rightarrow H_2O_2 + O_2$	(Ar), (N_2), (O_2), (Air)
$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2$	(Ar), (N_2), (O_2), (Air)
$2H_2O \rightarrow H_2O_2 + H_2$	(Ar), (N_2), (O_2), (Air)
$2H_2O + e^- \rightarrow H_2O_2 + H_2 + e^-$	(Ar), (N_2), (O_2), (Air)
$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2$	(Ar), (N_2), (O_2), (Air)
$HO_2^{\bullet} + H^{\bullet} \rightarrow H_2O_2$	(Ar), (N_2), (O_2), (Air)
$2H_2O + e^- \rightarrow H_2O_2 + 2H^{\bullet} + e^-$	(Ar), (N_2), (O_2), (Air)
$H_2 + O_2 \rightarrow H_2O_2$	(Ar), (N_2), (O_2), (Air)
HNO_2	
$HO_2 + NO_2 \rightarrow HNO_2 + O_2$	(N_2), (Air)
$NO_2^- + H^+ \rightarrow HNO_2$	(N_2), (Air)
HNO_3	
$NO + HO_2 \rightarrow HNO_3$	(N_2), (Air)
$3NO_2 + H_2O \rightarrow NO + 2HNO_3$	(N_2), (Air)
$ONOO^-$	
$OH^{\bullet} + NO_2^{\bullet} \rightarrow ONOO^- + H^+$	(N_2), (Air)
ONOOH	
$NO + HO_2 \rightarrow ONOOH$	(N_2), (Air)
$NO_2^- + H_2O_2 + H^+ \rightarrow ONOOH + H_2O$	(N_2), (Air)
NH_3	
$N + 3H^{\bullet} \rightarrow NH_3$	(N_2), (Air)
$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$	(N_2), (Air)
NH_4^+	
$NO_2^- + 8H^+ + 6e^- \rightarrow NH_4^+ + 2H_2O$	(N_2), (Air)
$NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$	(N_2), (Air)
$NH_3 + H^+ \rightarrow NH_4^+$	(N_2), (Air)
$NO_3^- + 4H_2 + 2H^+ \rightarrow NH_4^+ + 3H_2O$	(N_2), (Air)