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Effect of Storage Temperature on pH and Conductivity of Reverse Osmosis Water Treated with Atmospheric Plasma

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ABSTRACT: We believe that the reactions involved in plasma-activated water (PAW) production are a consequence of long-lived reactive oxygen and nitrogen species (e.g., NO, O, OH, $ONOO^-$, and H_2O_2) that are transferred from the plasma environment to liquid. Based on the assumption of reaction continuity in water treated with atmospheric plasma, we devised an experiment to monitor pH and electrical conductivity in samples of reverse osmosis water, before and after treatment. We used gliding arc discharge that was operated by a mixture of air + humid air at a flow of 10 L/min to evaluate the continuation of these chemical reactions at different storage temperatures: room temperature (24°C) for group 1 and refrigeration temperature (3°C) for group 2. To obtain PAW, we treated three 250-mL samples of reverse osmosis water for 10, 20, and 30 min of exposure to the plasma. After treatment, we performed periodic monitoring of the samples, with 24 h among measurements for a total period of 96 h. We can conclude that with increasing treatment time, acidification and electrical conductivity of water also increase. At this experiment range, storage temperature did not to exert significant influence on PAW physicochemical properties.

KEY WORDS: plasma-activated water, gliding arc, types of water

I. INTRODUCTION

Discharges in contact with or immersed in liquids are a rich source of highly oxidative and reductive radicals that provide a sustainable level of reactivity. Such discharges, consequently, induce chemical changes in the aqueous medium including decreased pH and strong oxidizing action.[1–3] The technique that produces plasma-activated water (PAW)[4] has gained importance in decontamination and disinfection.[5,6] Reactive oxygen and nitrogen species (RONS) that are generated in the plasma are transported in the liquid medium by convection and diffusion.[7] According to Verlackt et al.,[7] the dissolved species accumulate in an inverse vortex at the plasma–liquid interface and are then transported through the superficial to deepest layers of the liquid medium. RONS that are considered to be representative of oxidative reactions are hydrogen peroxide (H_2O_2), nitrite (NO_2^-), and nitrate (NO_3^-).[8]

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The complexity of PAW was first pointed out by Traylor et al.,[9] who concluded that the multiple chemical components present in PAW may exert different biological effects at different time scales. The authors corroborated this by concluding that to affect concentration of long-lived species, the chemistry involved needed longer time scales. They observed that short-lived species, that is, OH, NO_2, and NO_3, undergo significantly decreased densities every 1 mm at the plasma–liquid interface and are completely consumed in the liquid's lower layers. Other species, including H_2O_2, HNO_2/NO_2^-, NO_3^-, HO_2/O_2^-, O_3, and $ONOOH/ONOO^-$, remain at their relatively constant densities as a function of greater interface distance.[7]

Storage conditions may also influence action time of PAW. Shen et al.[10] evaluated antimicrobial activity of PAW stored at different temperatures and found that PAW stored at –80°C maintained its bactericidal activity, unlike others that were stored at 25°C, 4°C, and –20°C, for which antimicrobial action decreased. On the basis of these findings, our objective was to monitor pH and electrical conductivity of reverse osmosis water samples after treatment with atmospheric plasma at different storage temperatures.

II. MATERIALS AND METHODS

A. Gliding Arc Reactor and Treatment Conditions

To obtain PAW, samples containing 250 mL reverse osmosis water (we used a 20 MΩ, OS 20 LXE) (Gehaka; São Paulo, Brazil) were exposed to plasma for different periods of time. Treatment groups were designated as control (without treatment) and treated. The treatment group varied in plasma exposure time of ~ 10 (T10), 20 (T20), and 30 (T30) min. We used a gliding arc type of reactor, previously described in studies by Doria et al.[11] and Simomura et al.[12] For treatments, we used gas composed of a mixture of compressed air (using the medical odontological compressor MSV 6/30) (Schulz SA; São Paulo, Brazil) that we passed through a Büchner flask containing deionized water. Flow rate was 10 L/min, and all treatment was performed in the discharge region. Figure 1 illustrates the treatment scheme.

B. pH and Conductivity

A properly calibrated pH meter (Q402M, QUIMIS; São Paulo, Brazil) was used for pH measurements (measurement range was from 0.00 to 14.00 pH, and a +2000-mV absolute) and conductivity (reading range was from 2 μS/cm to ~ 10.00 mS/cm) during a period of 96 h. To identify instantaneous effects of treatment, measurements were performed immediately before and after treatment and afterwards, with periodic monitoring at a 24-h intervals among measurements.

C. Storage

The samples were divided into two groups and subjected to two storage temperatures: room temperature (24°C) and refrigerated temperature (3°C). Vials were packed with

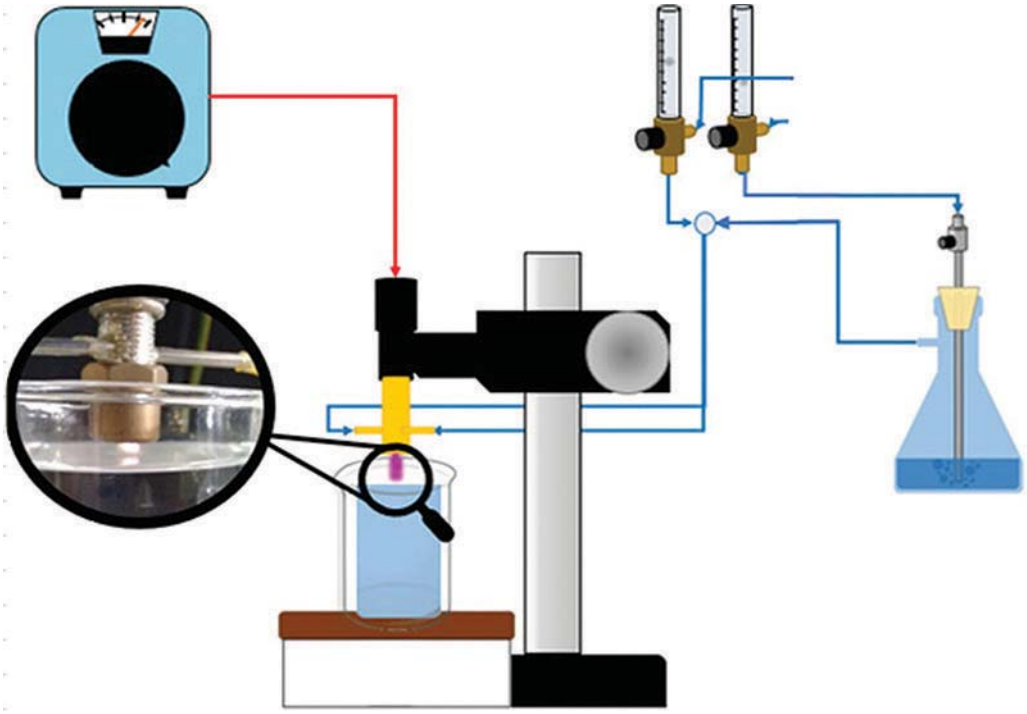

FIG. 1: Sample treatment scheme

aluminum foil to ensure that samples were only exposed to plasma discharge and no other source of energy.

D. Statistical Analysis

Statistical analyses were carried out using analysis of variance (ANOVA), using R software, version 3.2.3 (R Foundation for Statistical Computing).

III. RESULTS

Results obtained after treatment and during subsequent storage for 96 h are shown in Table 1. Behavior of groups during the 24-h periodic monitoring is presented in Fig. 2. ANOVA results are shown in Fig. 3.

When evaluating how group pH and conductivity were affected at the end of the experiment (Table 1), we found that storage temperature did not seem to exert a significant influence. However, periodic monitoring during the 96 h of storage (Fig. 2) indicated that pH during the 48–72-h storage interval tended to return to a neutral pH. This is most evident in the T20 group, in which the refrigerated temperature (3°C) seemed to accentuate this behavior.

TABLE 1: Averages of pH and conductivity after 96 h of storage

	Control		T10		T20		T30	
Average	**pH**	**µS**	**pH**	**µS**	**pH**	**µS**	**pH**	**µS**
Stored at 24°C	6.96	10.8	6.49	19.42	5.50	26.41	6.37	309.14
Stored at 3°C	6.71	11.08	6.15	19.47	6.13	27.53	6.24	134.30

T10, 10 min; T20, 20 min; T3: 30 min.

Regarding conductivity, treated groups followed the control variable, and only the T30 group showed a behavioral difference. It should be noted that the sudden increase in conductivity at 72 h of storage at room temperature was due to the isolated result of one of the samples, for which the specific value reached 642 µS/cm^2. Because this value was quite discrepant from previous and subsequent results, we concluded that it was likely an outlier.

ANOVA results in Fig. 3 reveal the significance of factors including treatment, storage time (Tp), and storage temperature (Tt) on pH and conductivity, including the possible interaction among these factors, with two-to-two interaction and all three together, as follows: T:Tp, interaction between treatment and time after treatment; T:Tt, interaction between treatment and temperature; Tp:Tt, interaction between time after treatment and temperature; and T:Tp:Tt, interaction among the three factors.

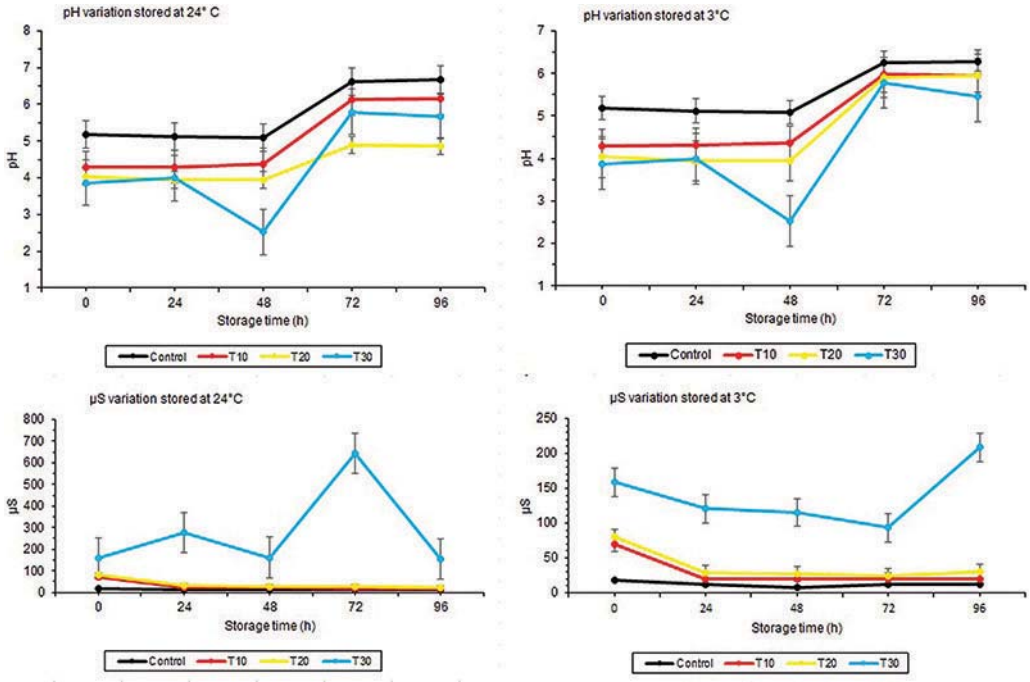

FIG. 2: pH and µS variation with storage at 24°C and 3°C

> ANOVA pH (T10min)						> ANOVA µS (T10min)					
	Df	Sum Sq	Mean Sq	F value	Pr(>F)		Df	Sum Sq	Mean Sq	F value	Pr(>F)
T10	1	2.765	2.765	16.978	0.000156 ***	T10	1	3.662	3.662	20.552	0.000853 ***
Tp1	1	10.683	10.683	65.591	2.12e-10 ***	Tp1	4	16	4	0.023	0.998801
Tt1	1	0.408	0.408	2.508	0.120135	Tt1	1	181	181	1.017	0.33488
T10:Tp1	1	0.090	0.090	0.555	0.459928	T10:Tp1	-	-	-	-	-
T10:Tt1	1	0.090	0.090	0.551	0.461834	T10:Tt1	1	66	66	0.372	0.554517
Tp1:Tt1	1	2.150	2.150	13.203	0.000702 ***	Tp1:Tt1	3	12	4	0.023	0.995064
T10:Tp1:	1	0.067	0.067	0.411	0.524561	T10:Tp1:	-	-	-	-	-
Residuals	46	7.492	0.163			Residuals	11	1.960	178		
> ANOVA pH (T20min)						> ANOVA µS (T20min)					
	Df	Sum Sq	Mean Sq	F value	Pr(>F)		Df	Sum Sq	Mean Sq	F value	Pr(>F)
T20	1	11.929	11.929	143.814	9.28e-16 ***	T20	1	6.798	6.798	38.149	6.94e-05 ***
Tp2	1	13.246	13.246	159.698	< 2e-16 ***	Tp2	4	47	12	0.066	0.991
Tt2	1	0.668	0.668	8.057	0.00672 **	Tt2	1	126	126	0.708	0.418
T20:Tp2	1	0.451	0.451	5.441	0.02410 *	T20:Tp2	-	-	-	-	-
T20:Tt2	1	3.084	3.084	37.179	2.07e-07 ***	T20:Tt2	1	103	103	0.575	0.464
Tp2:Tt2	1	2.234	2.234	26.934	4.64e-06 ***	Tp2:Tt2	3	88	29	0.165	0.917
T20:Tp2:	1	0.082	0.082	0.993	0.32416	T20:Tp2:	-	-	-	-	-
Residuals	46	3.815	0.083			Residuals	11	1.960	178		
> ANOVA pH (T30min)						> ANOVA µS (T30min)					
	Df	Sum Sq	Mean Sq	F value	Pr(>F)		Df	Sum Sq	Mean Sq	F value	Pr(>F)
T30	1	4.267	4.267	15.520	0.000275 ***	T30	1	216.830	216.830	1.216.753	1.29e-12 ***
Tp3	1	25.982	25.982	94.495	9.94e-13 ***	Tp3	4	155.961	38.990	218.797	2.11e-10 ***
Tt3	1	0.115	0.115	0.418	0.521168	Tt3	1	166	166	0.934	0.354604
T30:Tp3	1	4.535	4.535	16.493	0.000188 ***	T30:Tp3	-	-	-	-	-
T30:Tt3	1	0.359	0.359	1.307	0.258778	T30:Tt3	1	5.804	5.804	32.570	0.000137 ***
Tp3:Tt3	1	0.767	0.767	2.790	0.101675	Tp3:Tt3	3	253.725	84.575	474.598	6.52e-12 ***
T30:Tp3:	1	0.110	0.110	0.401	0.529953	T30:Tp3:	-	-	-	-	-
Residuals	46	12.648	12.648			Residuals	11	1.960	178		
Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1											

FIG. 3: ANOVA results. Tp, Storage time; Tt, storage temperature

IV. DISCUSSION

For the groups treated in the present study, ANOVA results produced evidence that treatment time was a statistically significant factor for both pH and conductivity. Storage time was significant for pH in all treatments, but conductivity was only significant for T30 treatment. Storage temperature was significant for pH in T20 treatment, but this did not produce a perceptible influence on conductivity.

Regarding the effect of interaction of two factors together, we observed that pH was not only affected by interaction of storage time and temperature, but also by interaction between treatment and storage time. Conductivity was affected by interactions only in the T30 treatment, in which an interaction between treatment and temperature was found as well as time and storage temperature.

With periodic monitoring (Fig. 2) immediately after treatment (time 0), it is possible to infer a direct relationship of proportionality between a reduction in pH and an increase in conductivity with time of exposure to plasma. This relationship has already been reported in studies with other plasma devices, with some summarized in Table 2.

TABLE 2: pH and conductivity of different plasma devices used to make PAW

Discharge type	Treatment time	pH	Conductivity	Ref.
Cylindrical double DBD	15 min	3.65 ± 0.01	32 ± 1 μS/cm	13
	30 min	3.15 ± 0.01	75 ± 2 μS/cm	
μ-Jet	0–50 min	2	1200 μS/cm	14
μ-Arc	0–50 min	2	2000 μS/cm	
Plasma jet	10 min	3	350 μS/cm	15
	20 min	3	450 μS/cm	

DBD, Dielectric-barrier discharge; PAW, plasma-activated water.

Increased conductivity and decreased pH are evidence of the accumulation of active ions in PAW.[13] According to Vlad and Anghel,[14] electrical conductivity and pH are dependent on the concentration of nitric acid in the water. These authors compared pH and electrical conductivity of the treated water with the plasma, using the pH and electrical conductivity of a solution of HNO_3. They noticed that both the HNO_3 solution and the treated water had similar values within the error range of the measurements. They suggested that both effects were caused by acidification, and increased electrical conductivity was due to the formation of NO_3/HNO_3 in water exposed to plasma.[14]

However, ANOVA also showed differences in influences of the other factors on the treated groups. For the T10 group, significant factors affecting pH, in addition to the time of treatment, included time after treatment (Tp1) and the interaction of two to two: time after treatment and temperature (Tp1:Tt1). If we compare with the results shown in Fig. 2, we can see that for up to 48 h, the T10 group presented the most linear pH of the treated groups. However, after 72 h of storage, the pH returned to neutral, a more pronounced characteristic when stored at refrigerated temperature. This supports the significance of the interaction Tp1:Tt1.

For the 20-min group, in addition to the factors that also influenced the 10-min group, storage temperature (Tt2) and its respective interactions were significant. The difference in pH behavior in groups stored at room temperature and those that were refrigerated is very evident (Fig. 2), because in the first condition, the variation for neutrality with 72 h is minimal. This is dissimilar to what is shown in the second condition, in which the pH of T20 arrives to the same value as that of T10. Finally, for T30, time after treatment (Tp3) and the respective interaction with treatment (T30:Tp3) were more significant. In 48 h of storage, pH became more acidic and then returned to neutral. It is possible that this difference was a consequence of the outlier sample that also influenced conductivity behavior.

V. CONCLUSIONS

Statistical analyses showed that in addition to treatment time, other factors influenced pH and conductivity of the samples subjected to plasma, and each factor contributed differently throughout the storage period. Monitoring the control group together with the treated groups showed a tendency to return from a more acidic to a neutral pH that is intrinsic to water. However, exposure to plasma caused treated groups to exhibit differences in pH levels over time and at the end of the experiment. A suggestion for future studies is to quantify the concentration of these long-lived reactive species in the water and assess whether storage factors may interfere with species production and consequent concentration.

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