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Physicochemical Properties of Plasma-activated Water by Corona Discharge Plasma in Liquid Electrodes System

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The aim of this work was to determine the effects of positive and negative corona discharges on the chemical and physical properties of tap water activated at atmospheric pressure in a liquid water electrode system. The properties of tap water include pH, TDS, electrical conductivity, temperature, and the stability of active species in the solution of nitrate (NO_3), nitrite (NO_2), and hydrogen peroxide (H_2O_2). The results showed that the concentrations of NO_2, NO_3, and H_2O_2 increased with increasing applied voltage in the case of positive and negative corona discharges. The pH value of water showed different behaviors in the presence of negative and positive corona discharges. On the other hand, the behavior of other physical properties such as total dissolved solids (TDS), electrical conductivity (EC), and water temperature under applied voltage showed the same behavior in the presence of both types of corona discharges.

***Keywords*:** Corona discharge; Plasma Activated Water (PAW); Tap water; Water treatment
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1. Introduction

Plasma can be defined as an ionized gas consisting of neutral particles, electrons, and positive and negative ions that exhibit collective behavior [1]. There are two main types of plasmas, depending on the temperature of the plasma: thermal equilibrium plasma and non-thermal equilibrium plasma. Thermal equilibrium is a state in which all particles (including electrons, ions, and neutral particles) have the same temperature. On the other hand, non-thermal equilibrium refers to a state in which the temperatures of several parts of the plasma are different. In particular, the temperature of electrons is significantly higher than that of heavier particles such as ions, atoms, and molecules [2]. Both types of plasmas are used in different fields, such as surface treatment [3-6], thin film production [7-9], water treatment [10-12], plasma activated water [12-15], etc. In water treatment, corona discharge is used in water treatment to create activated water components. This type of discharge is a weak filamentary discharge that is continuously generated by a strong electric field around a wire, a small diameter needle, or the sharp edge of an electrode [11]. Discharges usually occur in high-voltage systems when the electric field strength around the electrode is high enough but not strong enough to cause electrical breakdown between adjacent terminals. This phenomenon has a wide range of applications [12,13]. Anyway, plasma activated water (PAW) is a new technology for treating water using low-temperature plasma [16]. This technology is one of the most important technologies in biological applications. As a result, many reactive oxygen species (ROS) and reactive nitrogen species (RNS), such as hydrogen peroxide (H_2O_2), singlet oxygen (O_2), ozone (O_3), nitrogen oxides (NO) and hydroxyl radicals (OH) as well as electrons, ions and photons are generated by cold atmospheric pressure plasma generated at or near room temperature. These characteristics make plasma very suitable for environmental and medical applications [14].

In this work the influence of types of Corona discharge on the tap water properties and concentration of active water species will investigated in more details.

2. Physicochemical Properties of Plasma-Activated Water

When plasma interacts with water, various reactive oxygen and nitrogen species (RONS) are formed at the gas-liquid interface [17]. These primary reactive species then react with water molecules and with each other, resulting in the formation of a variety of secondary species that are important for a variety of applications. The resulting reactive species can be divided into long-lived species such as hydrogen peroxide (H_2O_2), ozone (O_3), nitrite (NO_2^-), and nitrate (NO_3^-), which have half-lives ranging from minutes to days, and short-lived species such as hydroxyl radicals (OH), nitric oxide (NO), and peroxynitrite ($ONOO^-$), which have half-lives ranging from nanoseconds to seconds and react rapidly to form stable species [17,18].

RONS are created through a three-stage process:

(1) In the gas phase, the primary species (•OH, •NO, •H, •O, •N) are generated as free radicals with relatively short lifetimes of 1.3–2.7 μs. Due to their high reactivity, they easily react with other free radicals or nearby gases and produce secondary species such as H_2O_2, NO_2, NO_3 and O_3.

(2) At the gas-liquid interface, both primary and secondary species react with the evaporated water in the solution to produce various compounds such as ·OH, O, H, ·NO, HNO_3, O_3, H_2O_2, HNO_2, etc.

(3) In the liquid phase, the gaseous free radicals mix with the solution and react with H_2O to produce

compounds such as ONOOH, N_2O_5, HNO_3, $ONOO^-$, etc.

Figure (1) shows the formation of reactive oxygen and nitrogen species (RONS) during PAW growth [19,20].

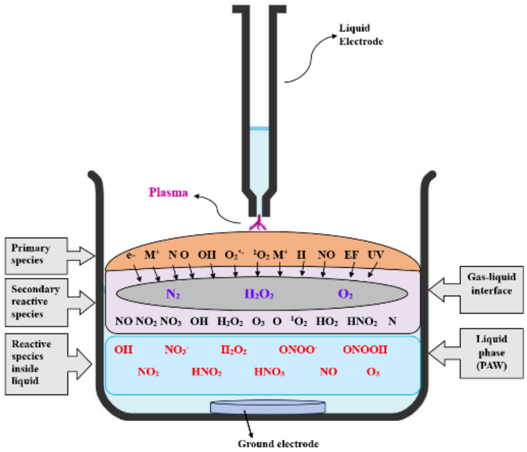

Fig. (1) The process of generating reactive species in PAW

2.1 Reactive Nitrogen Species (RNS)

As secondary products produced by PAW, nitrates (NO_3) and nitrites (NO_2) are both long-lived species. The type of plasma generator and treatment settings has an impact on the production of NO_2 and NO_3 in PAW. Creation and destruction pathways for the active constituents in PAM [21,22];

Reactive species	Creation pathways	Destruction pathways
Nitrate (NO_2)	$NO + O \rightarrow NO_2$	$NO_2 + OH \rightarrow ONOOH$
	$2NO + O_2 \rightarrow 2NO_2$	$HO_2 + NO_2 \rightarrow HNO_2 + O_2$
	$HNO_2 + OH \rightarrow H_2O + NO_2$	
	$HNO_2 \rightarrow NO_2^- + H^+$	
	$NO_2 + NO_2 + H_2O \rightarrow NO_2^- + HNO_3^- + H^+$	
	$NO_2 + O \rightarrow NO_3$	
	$NO_2 + O_3 \rightarrow NO_3 + O_2$	
	$HNO_3 \rightarrow NO_3^- + H^+$	
	$NO_2^- + O_3 \rightarrow NO_3^- + O_2$	
	$NO_2 + NO_2 + H_2O \rightarrow NO_2^- + NO_3^- + H^+$	
	$ONOOH \rightarrow NO_3^- + H^+$	
Nitrite (NO_3)		$NO + NO_3 \rightarrow NO_2 + NO_2$
		$NO_3 + NO_3 \rightarrow NO_2 + NO_2 + O_2$

2.2 Reactive Oxygen Species (ROS)

Hydrogen peroxide (H_2O_2) is the most prevalent long-lifetime species in PAW and plays a critical role in seed germination and antimicrobial activity. PAW primarily generates H_2O_2 through two pathways:

(1) OH radicals generated in the gas phase combine to form H_2O_2 and diffuse directly into the liquid phase, and

(2) OH radicals generated in the gas phase diffuse into the liquid phase and then combine to form H_2O_2 [19,22]

Hydrogen peroxide (H_2O_2)

$OH + OH \rightarrow H_2 O_2$ $\qquad$ $OH + H_2 O_2 \rightarrow HO_2 + H_2 O$

2.3 Physical Properties of Water

There are many water properties such as pH, total dissolved solids (TDS), electrical conductivity and water temperature will studied in this section;

a. pH: The pH value of water is a measure of its acidity or alkalinity. Therefore, its level indicates the activity of hydrogen [23]. Water pH is tested using pH units. As a logarithmic value, pH represents the concentration of hydrogen ions, or [H^+], in the water. The water's acidity, or basicity, can be determined by its pH. It is convenient to express the concentration using a logarithmic scale since the concentration of [H^+] and [OH-] might fluctuate from 10^0 to 10^{-14}.

b. TDS are an essential property in the characterization of natural waters. TDS analysis is a measure of the amount of dissolved materials in the water in ppm or the equivalent mg/L. The purpose of this parameter is to evaluate and measure all suspended and dissolved matter in water [24].

c. Electrical conductivity (EC) refers to the ability of a solution to conduct electrical current. The conductivity value increases as the amount of dissolved substances in the water increases. EC is measured in mS/m units. Other units also used include PS/cm, which numerically equals to μmho/cm [25].

d. Water temperature: This refers to the temperature of the solution. It is often expressed in °C or °F.

3. Experimental Part

Figure (2) shows schematically the experimental setup of the liquid electrode system. The setup included a high-voltage DC power source with a maximum high voltage of 45 kV and a cylindrical glass vessel with a volume of 500 cm^3 which is filled by tap water with volume of 100 cm^3 that used as liquid electrode (which represents the active electrode). The end of the glass vessel near from water surface was sealed with capillary tube with diameter of 0.07 mm where the water drop formed in the end of the capillary tube. The other electrode is circular aluminum disc with diameter 4 cm which is immersed inside the liquid tap water. The air gap between the liquid electrode and water surface is 1 cm where the both corona discharge formed in it. The corona discharge is produced in the gap air by applying a high voltage between a liquid electrode and the water's surface. The corona discharge images are captured by an iPhone 15 pro max camera with a resolution of 2796x1290.

The water properties was measure used a CyberScan PC 300 to measure pH, TDS, EC, and water temperature. The reactive oxygen and nitrogen species (RONS) were measured using American Bartvation kits. To measure the concentration of NO_2 and NO_3, the test strip must be dipped into the solution for 2–3 s, removed, shaken to remove excess liquid, and after the 30s, compared to the color chart. As shown in Fig. (3a), the H_2O_2 kits can be used by dipping a test strip into the solution for 1s and removing it. The test pad should be shaken to remove the excess liquid after 10 s compared to the color scale (see Fig. 3b,c).

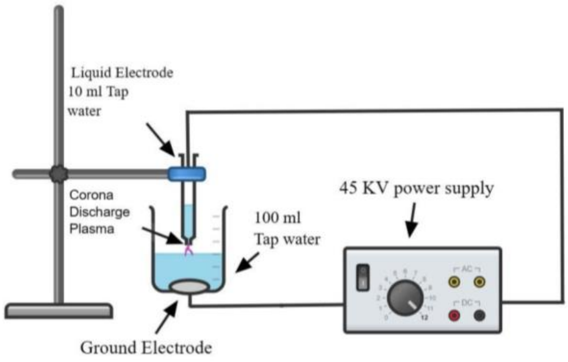

Fig. (2) Schematic diagram of the liquid electrodes system

(a) (b) (c)

Fig. (3) (a) The strips used (nitrite 0–25 ppm, nitrate 0–500 ppm), (b) Hydrogen peroxide H_2O_2 test strips low level [0–100 ppm]), (c) Hydrogen peroxide H_2O_2 test strips high level [100–400 ppm])

4. Results and Discussion

Figure (4) illustrates the effect of high pressure on the negative corona discharge formed at the tip of a capillary in an air gap above the water surface at atmospheric pressure. It can be observed that the water droplet formed at the end of the capillary expands in a conical shape. The intensity of the negative corona discharge increases with increasing applied voltage, while the cone size decreases with increasing applied voltage. As the applied voltage increases, the ionization region appears to be very close to the active electrode and extends to the water surface. The increase in applied voltage leads to an increase in the number of corona branches near the active liquid electrode.

In addition, the effect of applying high voltage on the positive corona discharge at atmospheric pressure is also observed in Fig. (5). This image also examines the increase in the intensity of the positive corona discharge near the active water electrode at the end of the capillary. In addition, as the applied voltage increases, the corona discharge is divided into many branches.

In summary, by comparing figures (4) and (5), it can be seen that the intensity of the negative corona discharge is higher than that of the positive corona discharge. This behavior can be due to the increase of the high negative applied voltage causes sharply increase of the electric field of the drift region of the negative corona discharge (i.e., increasing the electron/negative ion ratio) comparable with positive corona discharge [26].

In this section, the effect of higher applied voltage on the physical properties of tap water is investigated. Figure (6) shows the effect of high voltage of two types of corona discharge on the pH value of tap water at a constant treatment time of 20 minutes. From this figure, it can be seen that the behavior of pH value when voltage is applied is different depending on the type of corona discharge. This behavior means that changing the polarity of the discharge causes different chemical reactions in the water.

In addition, figure (7) shows the change of TDS at higher applied voltages for corona discharges of different polarities. The data show that both types of corona discharges cause the TDS value of water to increase with increasing applied voltage, but at different rates. This behavior can be attributed to the fact that the corona discharge formed in the air gap causes many reactions in the water and increases the salt concentration in the water.

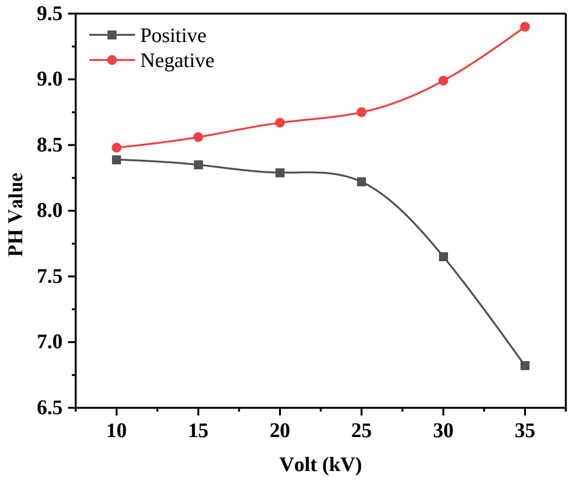

Fig. (6) Variation of pH value as a function of applied voltage of the positive and the negative corona discharges at atmospheric pressure

According to Fig. (7), the electrical conductivity (EC) of tap water increases with increasing applied voltage in both types of corona discharge (see Fig. 8). The measured conductivity value increases significantly due to changes in water structure caused by increased solute concentration and different chemical reactions depending on the type of corona discharge.

Vol. 21, No. 1, January-March 2025, pp. 105-112

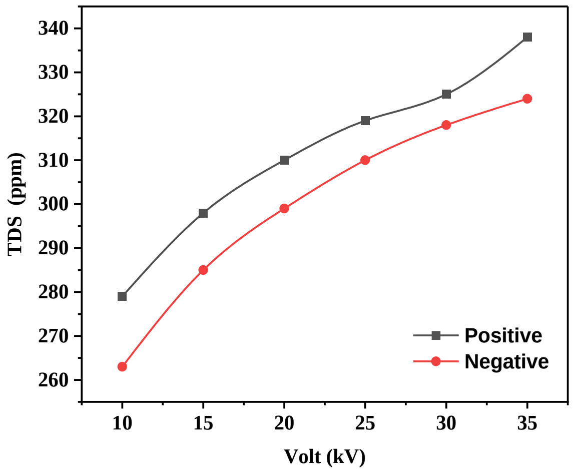

Fig. (7) Variation of TDS as a function of the applied voltage of positive and negative corona discharges at atmospheric pressure

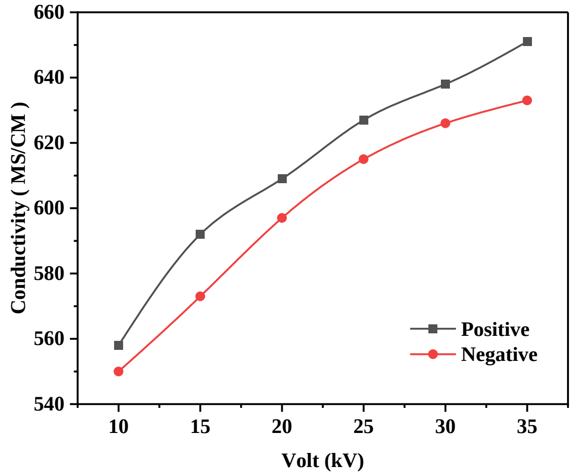

Fig. (8) Change in electric conductivity (EC) as a function of the applied voltage of the positive and negative corona discharges at atmospheric pressure

Finally, the variation of tap water temperature with applied voltage can also diagnose the two types of corona discharge, as shown in Fig. (9). From this figure, it can be seen that the formation of both types of corona discharges leads to chemical reactions in the water, which are supported by the generated heat. In addition, the heat value supported by the negative corona discharge is higher than the heat value generated by the positive corona discharge. It can be concluded that the negative corona discharge is more active than the positive corona discharge.

The plasma-activated water (PAW) represents the water that has been treated with atmospheric pressure discharge. This section showed how the higher applied voltage effect on the concentration of NO_2, NO_3, and H_2O_2 at exposure time of 20 min in the presence of both corona discharges at atmospheric pressure (see Fig. 10). The results investigated that the concentrations curve was divided in two regions with increases of applied voltage. The first one shown sudden increases of all active species concentrations in the applied voltage range 10-25 kV. While the second section appear when the applied voltage above of 25 kV where the concentration of all active species become constant, where highest concentration appear in the voltage range of 25–35 kV. This is due to the significant impact of space charge in these voltage ranges for both types of corona discharge, as well as the differences in the half-lives of these active components. This results agree with references [21,27].

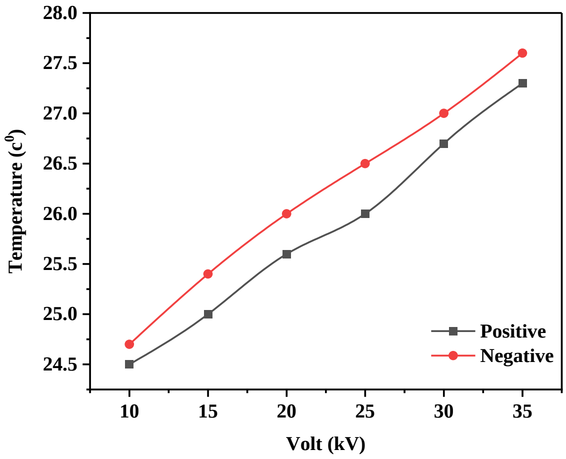

Fig. (9) Change in water temperature versus applied voltage of positive and negative corona discharge at atmospheric pressure

The variation of NO_2, NO_3 and H_2O_2 concentrations with storage time was investigated, which was established by a constant applied voltage of 35 kV. Tables (1) and (2) show the variation of NO_2, NO_3 and H_2O_2 concentrations with storage time in the presence of two types of corona discharge at atmospheric pressure.

A number of characteristics can be observed from these tables: The concentrations of NO_2, NO_3 and H_2O_2 decrease with increasing storage time. During negative corona discharge, the concentrations of these active substances remain stable within 24 h, whereas when positive corona discharge is applied, the concentrations of the active substances examined decrease to half of their initial values after 1 h of storage. Moreover, after 238 h (9 days), the concentrations of all active substances decrease to very low levels. This behavior is influenced by the half-life of the active substances. Similar results were also reported by Vlad et al. [28] who reported that nitrates remain stable in solution within 20 days after treatment. This is also consistent with the results of Ferreyra et al. [29] who observed that the concentration of H_2O_2 decreased significantly after 24 h of storage, and the concentration of NO_2 decreased significantly after 24 h.

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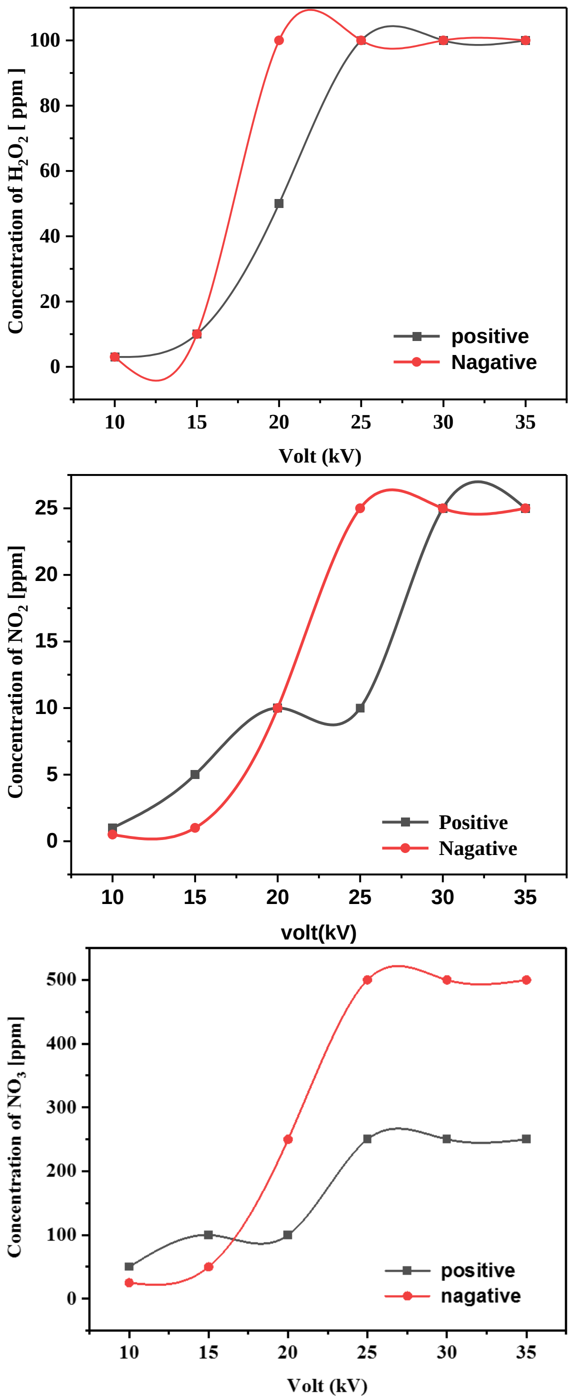

Fig. (10) Relationship between the concentration of H_2O_2, NO_2, and NO_3 and the applied voltage of positive and negative corona discharges at atmospheric pressure

5. Conclusions

This work investigates the effect of applied high voltage on the physicochemical Properties of tap Water when two types of corona discharge were formed in an air gap between an active liquid electrode and surface of tap water surface at atmospheric pressure. The data illustrated that the types of corona discharge has high effect on the physical properties of water and the concentrations of reactive species that formed in side water such as H_2O_2, NO_2, and NO_3. These reactive species has constant and higher concentration when the applied voltages range 25-35 kV. Furthermore, the concentrations of all reactive species that studied were higher in the presence of negative corona discharge comparable to the positive corona discharge. The life time of the reactive species that formed in the tap water is greater than in the presence of negative corona discharge than positive corona discharge.

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Table (1) Total concentrations of NO_2, NO_3, and H_2O_2 as a function of storage time for a 35 kV negative applied voltage

Negative 35 kV		Treatment time 20 minutes			
Storage time (hour)	NO_2 (ppm)	NO_3 (ppm)	H_2O_2 [0-100] (ppm)	H_2O_2 [0-400] (ppm)	Total concentrations
0	25	500	100	200	825
0.5	25	500	100	200	825
1	25	250	100	200	575
1.5	25	250	100	200	575
2	25	250	100	200	575
6	25	250	100	200	575
9	25	250	100	200	575
12	25	250	100	200	575
18	25	250	100	200	575
24	25	250	100	200	575
36	25	250	100	0	375
48	25	250	50	0	325
65	25	100	10	0	135
72	25	100	10	0	135
90	25	100	10	0	135
96	10	100	10	0	120
120	10	100	3	0	113
144	10	100	0	0	110
190	10	100	0	0	110
238	10	50	0	0	60

Vol. 21, No. 1, January-March 2025, pp. 105-112

Table (2) Total concentrations of NO_2, NO_3, and H_2O_2 as a function of storage time for a 35 kV positive applied voltage

Positive 35 kV		Treatment time 20 minutes			
Storage time (hour)	NO_2 (ppm)	NO_3 (ppm)	H_2O_2 [0-100] (ppm)	H_2O_2 [0-400] (ppm)	Total concentrations
0	25	250	100	0	375
0.5	25	250	100	0	375
1	10	100	50	0	160
1.5	10	100	50	0	160
2	10	100	50	0	160
6	10	100	50	0	160
9	10	100	50	0	160
12	10	100	10	0	120
18	10	100	10	0	120
24	10	100	10	0	120
36	10	100	3	0	113
48	10	100	0	0	110
65	10	100	0	0	110
72	10	100	0	0	110
90	10	100	0	0	110
96	10	100	0	0	110
120	10	100	0	0	110
144	5	50	0	0	55
190	1	50	0	0	51
238	1	25	0	0	26

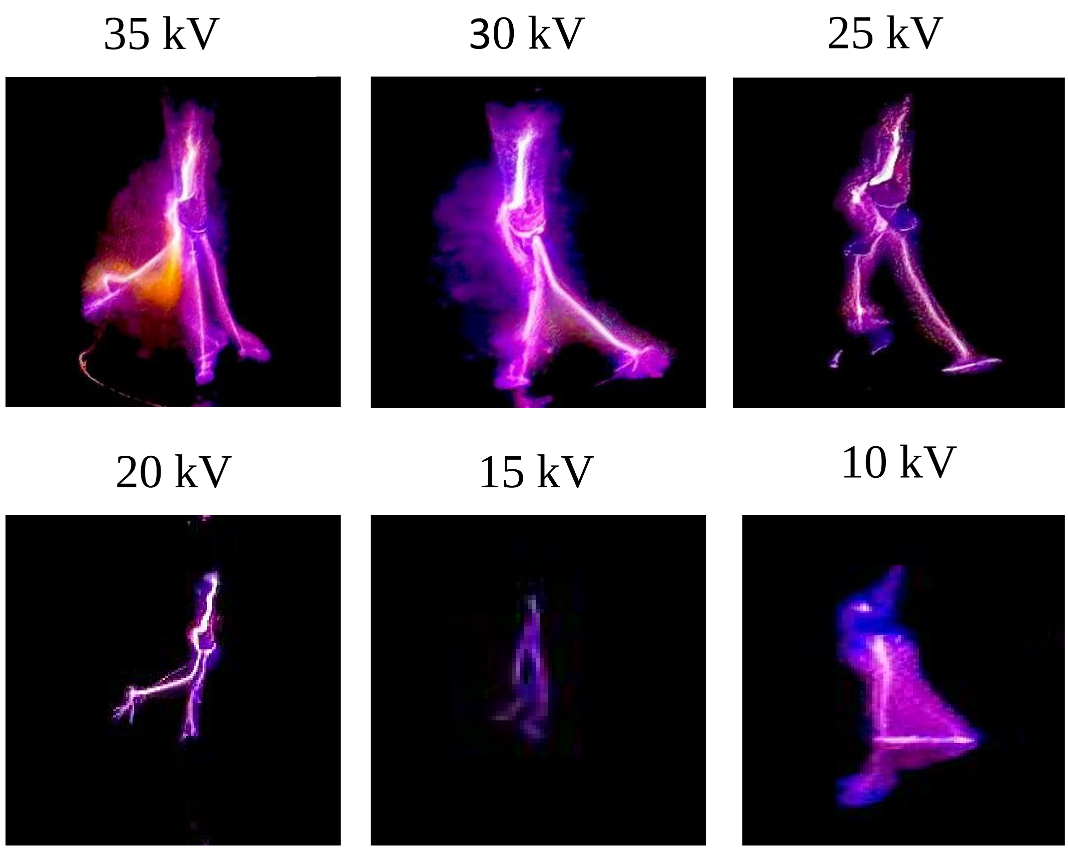

Fig. (4) Influence of applied voltage on the negative corona discharge in liquid electrodes system

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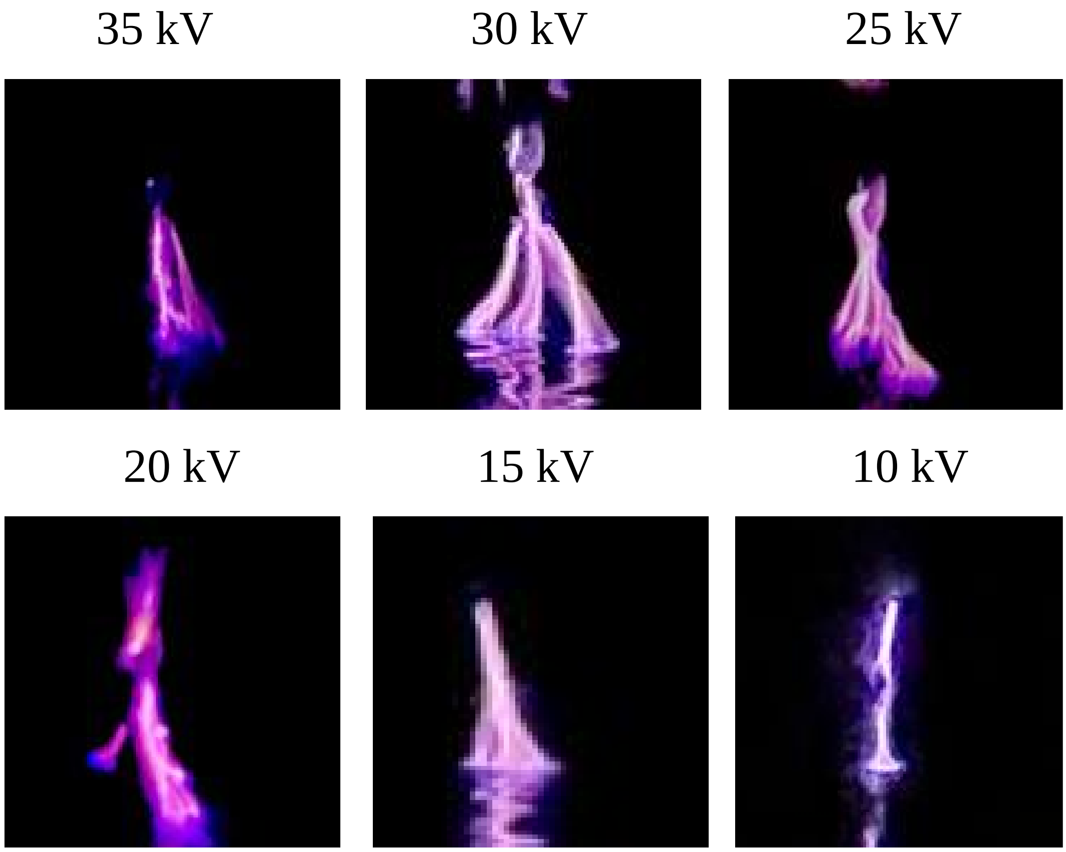

Fig. (5) Influence of the applied voltage on the positive corona discharge in liquid electrodes system

