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Verification and Demonstration of the Ability of Plasma Generated from Dielectric Barrier Discharge to Oxidize

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Abstract

The oxidation ability of cold plasma is a major influence on bacterial inactivation, lipid oxidation, medical equipment sterilization, and applications in air and wastewater purification, for this reason, the ability of cold plasma to oxidize materials is an important factor that must be studied. In this study, the ability of cold plasma generated by a dielectric barrier discharge (DBD) to oxidize materials was revealed and proven by using different exposure times (5, 10, 15, 20 min) and several measurements: the decolonization of indigo carmine from dark blue to yellow, the significant reduction in pH, and the increase in oxidation reduction potential (ORP) and electrical conductivity (EC), Proven spectrophotometrically in the presence of nitrogen and its oxide ions. It was observed that the exposure time of 15 min is the maximum period during which oxidation occurs, after which saturation occurs. Numerous reactive oxygen and nitrogen species are created upon the interaction of gas phase plasma and water vapor (supported by excited species, energies and plasma electrons).

Keywords: Dielectric barrier discharge **(**DBD), Decolorization, Electrical conductivity EC, Indigo carmine, Oxidation.

Introduction

Cold plasma is regarded as among the most modern technologies for sophisticated oxidation, cold plasma finds application in the fields of wastewater treatment and air purification, as well as in the treatment of various pollutants[1,2], sterilizing medical equipment[3], lipid oxidation[4], biodecontamination[5], and others[6,7]. Consequently, to maximize the chemical and biological effects of atmospheric non-thermal plasma discharges, research into the oxidation capacity of atmospheric plasma discharges is necessary.
The presence of nitrate and nitrate, a decrease in the medium's pH, an increase in conductivity, and chemical degradation are some indicators of plasma discharge's ability to oxidize. Nonthermal plasma can generate both oxidative and reductive radicals. There are several types of systems for generating nonthermal plasma such as DBD [8], FE-DBD [9-11], plasma jet [12], and microwave plasma [13].
A sophisticated oxidation process used to break down organic molecules in water is called non-thermal plasma (NTP). Whereas the exact chemical constitution of air, cold plasma discharge remains unclear, it is known that these discharges produce reactive oxygen species, and highly oxidizable nitrogen compounds. When the plasma interacts with the surrounding air, ionized air produces RONS. Delivery to the target, tissue, or fluid is what RONS are. At first, it was believed that RONS were the root cause of free radical aging[6]. Nonetheless, it is widely acknowledged that the therapy of disease may benefit from the use of exogenous RONS in small

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amounts. Several investigations have suggested a potential connection between angiogenesis, migration, apoptosis, and plasma-generated RONS in cell culture conditions.[14-17].

The oxidation effects of impulsive plasma discharge have been studied in this research. Surface discharges spread across an interface between liquid and air., while indirect discharges propagate through the liquid sample's bulk. The oxidizing capability was analyzed by estimating the degree of decolorization of IC dye in water solutions, Indigo carmine was chosen to serve as a chemical sensor. Numerous elements significantly contribute to these processes, including: reducing pH, oxidation reduction potential (ORP), Electrical conductivity (EC), concentration and transmittance of solution which are responsible for the oxidizing effect in principle.

In this paper, DBD is used to obtain cold plasma to investigate its chemical oxidation, a plasma oxidation process involves the use of active neutral and charged oxygen species to oxidize surfaces by discharging the ambient air, dielectric barrier discharges (DBDs), an advanced oxidation technology based on free radical processes, have been found to completely decompose. At the interface between gas and liquid, the NTP discharge caused the transient species (OH, O, and NO radicals) to develop. The indirect discharge treatment by using dielectric barrier discharge (DBD) possesses an efficiency of oxidation. The main effect that can be observed visually is the decolonization rate of indigo carmine, other factors related to the impacts on the chemical characteristics of the water that’s a laboratory measured, such as pH, oxidation reduction potential (ORP) and electrical conductivity (EC)

Materials and Methods

Dielectric barrier discharge system

DBD system is used to generate cold plasma to study the mechanism of oxidation capability of cold plasma, it consists of two electrodes made from stainless steel covered by Teflon and the quartz barrier between the electrodes as shown in Fig 1

Figure 1. high voltage Dielectric barrier discharge system.

The system was energized using a high voltage AC power supply, the magnitude of applied voltage about (15 kV), and consisted mainly of high-voltage electrodes, the cold plasma was obtained by ionizing the ambient air and applied on the sample for different times of exposure 0, 5, 10, 15, 20 min, and the electrode was separated from the solution surface by (2-3 mm) for discharge and plasma generation.

Indigo carmine

Indigo carmine pigment (IC) served as a chemical sensor for examining the cold plasma's ability for

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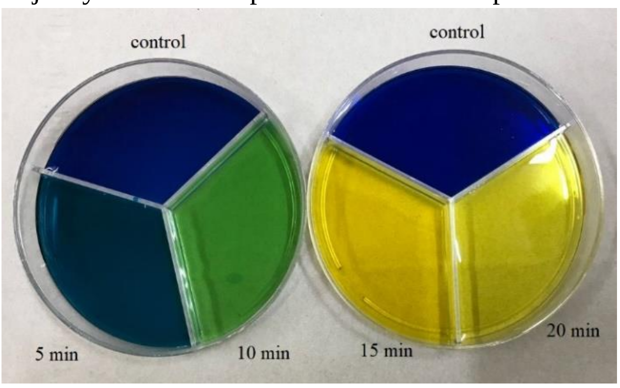
oxidation. Indigo carmine is a food coloring and safe to use, nontoxic, a powder is typically a dark blue. The formula of IC is (C16H8N2Na2O8S2), the molecular weight is 446.35 g/mol [18]. The solution was prepared by using deionized water to obtain a solution with concentration (0.35 mM) and pH 5.5. An essential component in assessing a solution's efficacy is its pH of non-thermal plasma oxidation in the medium. The pH, EC, ORP were measured by (PH-2603). The optical emission and transmission of the solution were measured by UV-visible spectrophotometer (SEC 2000 spectra system). The solution should be stored in a cool, dark place.

Results and Discussion

Oxidation effect on coloring, pH, electric conductivity, ORP of IC.

The study examined the oxidizing impacts of transient discharges that propagate through the majority of the sample. A 10 mL sample of IC solution was put into a Petri dish and exposed to plasma for each separate time, just like with the surface discharges. (0, 5, 10, 15, 20 min), the color was changed gradually from dark blue to green yellowish as shown in Fig 2.



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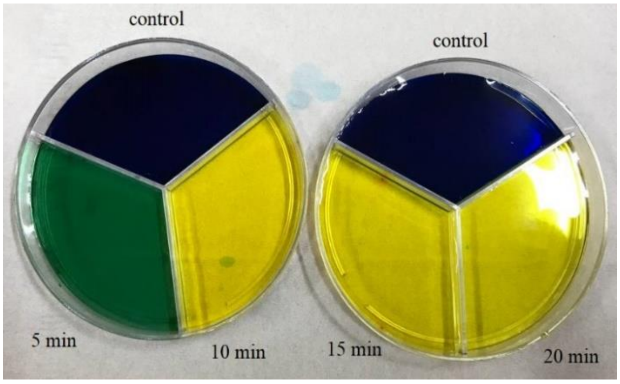

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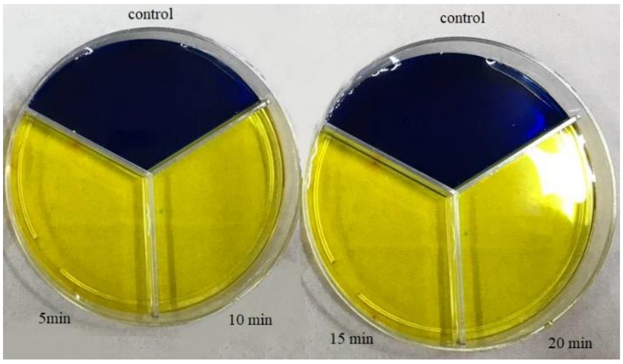

(c)

Figure 2. Decolorization of indigo carmine for different time of exposure to cold plasma and for different days a): 0-day, b) 1day, c) 3 days.

We show that the color of indigo solution changes after being exposed to plasma, initially transferring to dark green after 5 min of cold plasma exposure, then becoming light green after 10 min of plasma, and after 15,20 min turning to yellowish, the oxidation or acidic effect of the decrease in pH caused to change color from blue to yellow as shown in Fig 2. a).

After 24 hours of exposure, the color of the solution that's exposed for 5 min becomes light green, and the

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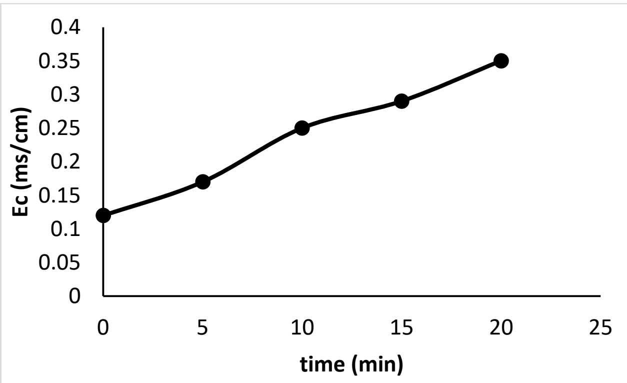
sample exposed for 10, 20 min it becomes yellow, as shown in Fig 2(b). Finally, after 72 h, the color of IC solution for all time becomes yellow for all time, which proves the lifetime of the plasma effect is long and not temporary. The reason for this behavior is due to the ability of plasma to oxidize, and it is considered a preliminary indicator to prove the ability of plasma to oxidize, it agree with [19] .

The electrical conductivity, pH, and oxidation reduction potential of the pigment solutions were measured before and after plasma treatment. An improvement in the solutions' electrical conductivity from 0.12 to 0.34 ms/cm was observed as shown in Fig. 3.a and an increase in ORP, the ORP measurement is related to the oxidation potential and formed the main species from non-thermal plasma as shown in Fig 3.b. A drop in the pH of aqueous dye solutions was seen in all treatment cases, which could be the result of nitric and nitrous acid production, coming from the formation of the nitrogen and its compounds nitrate and nitrate, non-thermal plasmas can activate the reactants N2 and H2/H2O, which then break down into reactive species like N, H, and OH radicals. These reactive species will eventually recombine to form intermediate compounds and NH3 as indicated by Eqs. (8-19) [19-21] Significantly, with increasing oxidation, the pH decreased from ~5.5 to a minimum value of ~3.18 as shown in Fig 3.c. All these indicate an oxidation effect and agree with [22, 23].



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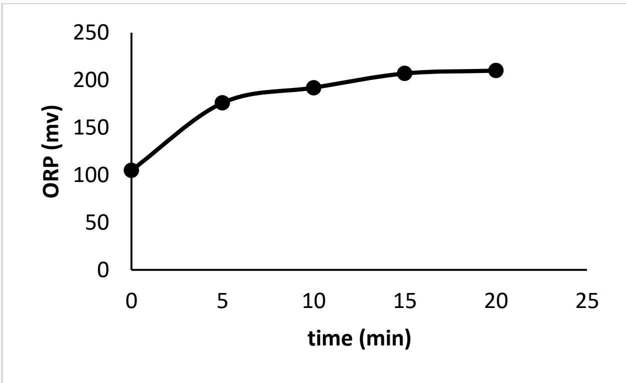

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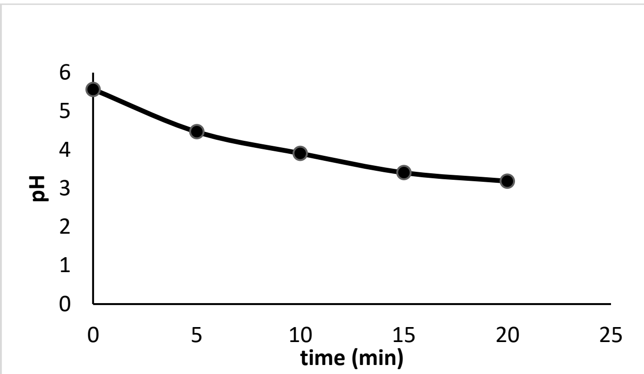

(c)

Figure 3. effect of cold plasma on a), conductivity b) ORP, c) pH.

The initial sample solution that was not exposed was tested as a reference. The control sample in this instance was distilled water. Fig 4a illustrates how the unexposed sample's transmittance differs from that of distilled water. The transmittance (T%) is less than 100% in the visible range which agrees with 23. This indicates that, in comparison to pure water, the IC solution has a reduced transmittance. Otherwise, a greater amount of visible light is absorbed by the IC sample solution.

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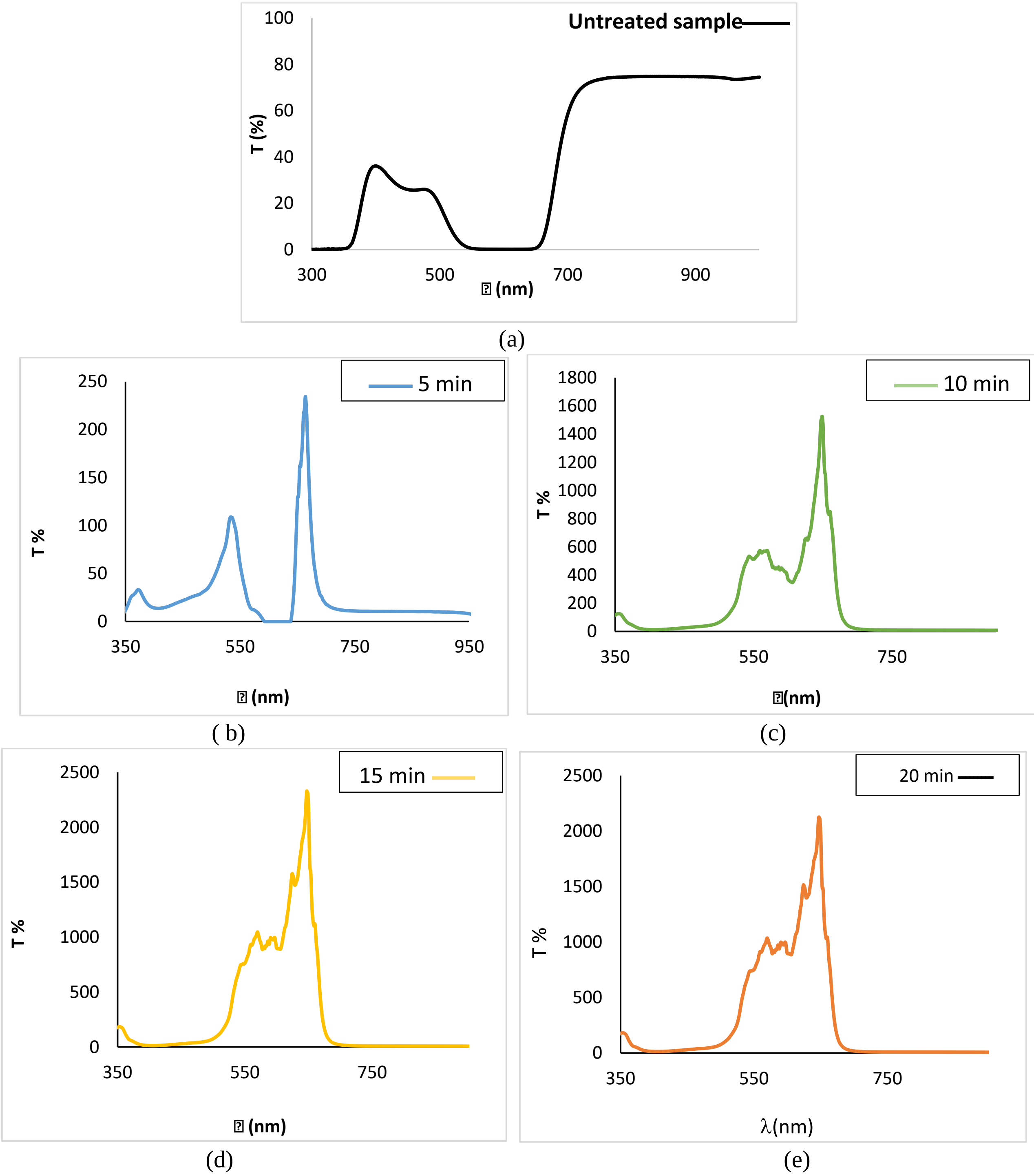

Figure 4. the transmission of Indigo solution before and after exposed to cold plasma a) untreated b) 5 min. c) 10 min. d) 15 min. e) 20 min.

Next, the exposed sample for plasma is utilized as the target sample, and the original unexposed IC solution is used as the control sample if the transmittance is less than 100%. One measures the differential transmittance spectrum. Two instances of the differential transmittance spectra of the "exposed sample to unexposed sample" were exposed to 5, 10.15, and 20 min. The transmission increased gradually after 5 min and the peak shifted into blue green region about 452- 539 nm as shown in Fig 4 b, while after 10 min the transmittance rose and the peak shifted to a green region (550 nm) as shown in Fig 4 c, even though 15 and 20 min a raised to same result as shown in Fig 4 d, E that means the solution

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reached to saturation after 15 min, the transmittance shifted to yellow region (586nm). As a result to change the pH the color may be change from blue to yellow. Consequently, since this is the wavelength range where blue to yellow light falls, it is important to look into changes in the wavelength of the differential spectrum between 450 and 590 nm, its agree with[24].

Optical emission analysis

Fig 5 represents the emission spectroscopy of CAP by DBD for the wavelength (250-500 nm), the reactive species produced by the DBD system are shown in the spectrum. The reference [16] was followed to identify the emission bands. It can be seen that modest emission bands for NO lines were found in the 250–300 nm wavelength range [16-17]. The direct electron impact excitation is responsible for the dispersion of the $N_2(C_3\Pi_m)$ excited state (having enough energy to pass the threshold) from the ground state N_2 $(X_1\Sigma_g +)$. The characteristic photons of the second positive band head (0-0) with a wavelength of 337.1 nm are released by the following radiative decays. The wavelengths of 315.29, 337, 358, and 380.4 nm could be analytic of the low-intensity N_2 second-positive system. $N_2\,(C_3\Pi_u)\; v\,'=0 \Longrightarrow N_2\, B\; _3\Pi_g\; v\,''=0$ 1

The dominant nitrogen spectrum lines are 315.29 nm to 470 nm The posterior radioactive degradation of distinct photons is dissolved from the second positive-band header (0-0) and has a wavelength of 337 nm

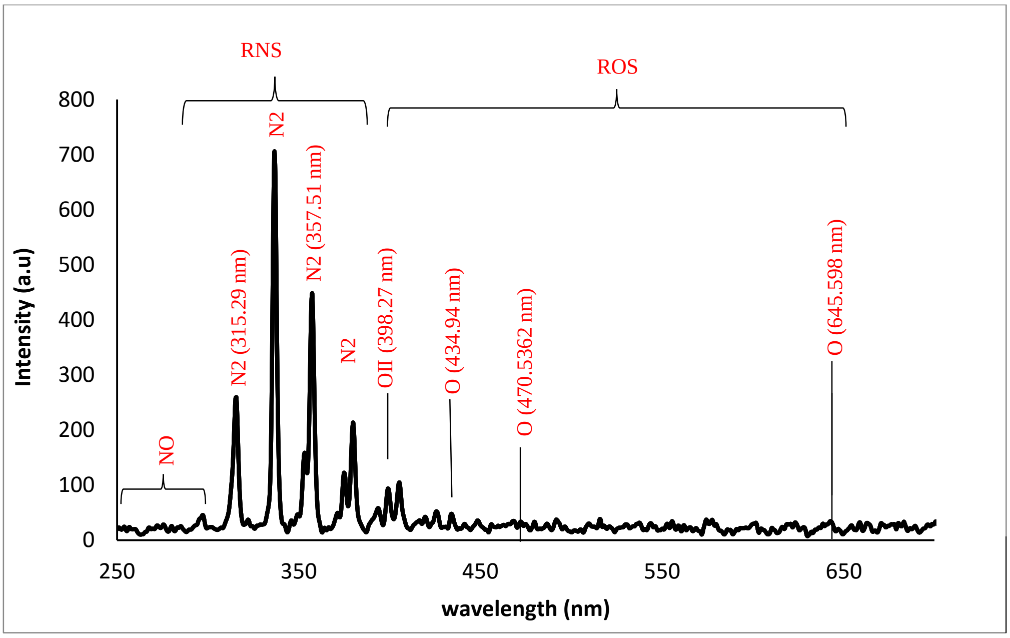

Figure 5. optical emission spectrum of cold plasma by DBD.

Consequently, the species has been identified in Fig 6 produced at the cold plasma gas-liquid interface; the primary species generated by cold plasma migrate by diffusion to the liquid phase and then stabilized by water forming the secondary species[24] as shown in Fig 6

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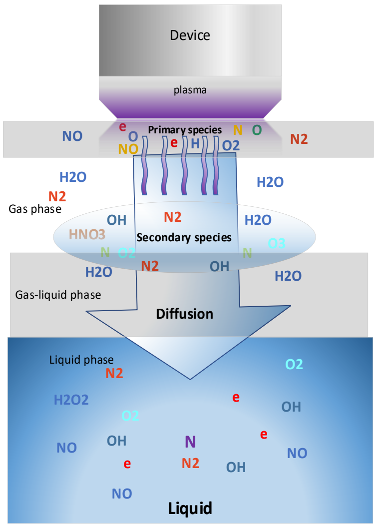

Figure 6. Reactive species production in plasma discharge, gas phase, gas–liquid phase, and liquid phase represented graphically.

$$H_2O + e^- \rightarrow H^{\cdot} + OH^{\cdot} \ldots\ldots 2$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \ldots\ldots 3$$

$$H_2O + e^- \rightarrow H_2O^+ + 2e^- \ldots\ldots 4$$

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH^{\cdot} \ldots\ldots 5$$

$$O_2 + O \rightarrow O_3 \ldots\ldots 6$$

$$2O_3 + H_2O_2 \rightarrow 3O_2 + HO^{\cdot} \ldots\ldots 7$$

$$N_2 + e^- \rightarrow N^{\cdot} + N^{\cdot} \ldots\ldots 8$$

$$N_2 + O \rightarrow NO^{\cdot} + N^{\cdot} \ldots\ldots 9$$

$$N^{\cdot} + O_2 \rightarrow NO^{\cdot} + O \ldots\ldots 10$$

$$NO^{\cdot} + O^{\cdot} \rightarrow NO_2 \ldots\ldots 11$$

$$NO_2 + OH^{\cdot} \rightarrow HNO_3 \ldots\ldots 12$$

$$NO^{\cdot} + N^{\cdot} \rightarrow N_2 + O \ldots\ldots 13$$

$$2NO^{\cdot} + O_2 \rightarrow 2NO_2 \ldots\ldots 14$$

$$2NO_2^- + 2H^+ \rightarrow NO^{\cdot} + NO_2 + H_2O \ldots\ldots 15$$

$$2NO_2 + H_2O \rightarrow 2NO_2^- + NO_3^- + 2H^{\cdot} \ldots\ldots 16$$

$$N + H \rightarrow NH \ldots\ldots 17$$

$$NH + H \rightarrow NH_2 \ldots\ldots 18$$

$$NH_2 + H \rightarrow NH_3 \ldots\ldots 19$$

Eqs. 2 to 19 [24-25] represented the products of a process known as indirect discharge, in which plasma generated in the gas phase comes into contact with water vapor and is assisted by both plasma electrons and the energies of excited species, produces a lot of reactive oxygen species in addition to nitrate, nitrite, and NO radicals.

Conclusion

The oxidation capability of cold plasma is a major influence on many applications such as inactivation of bacteria, lipid oxidation, sterilization of medical equipment, and applications in air and wastewater purification. Indigo carmine dye (IC) served as an effective chemical sensor for examining the cold plasma's ability for oxidation. It was shown that macroscope by decolorization of solution and microscope is done by measuring electric conductivity EC, pH, oxidation reduction potential (ORP) and optical emission spectroscopy and observed the main RONS species that produced, we show that the oxidation increased with increased time exposure for plasm by increased in EC, ORP and decreasing pH, and arrived to saturation time after 15 min from being exposed to cold plasma for 10 ml from solution.

Authors' Declaration

- Conflicts of Interest: None.
- I hereby confirm that all the Figures and Tables in the manuscript are mine. Furthermore, any Figures and images, that are not mine, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee at the University of Baghdad.

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اثبات وتوضيح قابلية البلازما المتولدة بتفريغ الحاجز العازل على الاكسدة

نور يعسوب عبد الخضر

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الخلاصة

إن قابلية البلازما الباردة على الاكسدة تلعب الدور الاساسي في قتل البكتيريا وأكسدة الدهون وتعقيم المعدات الطبية وتطبيقاتها في تنقية الهواء ومياه الصرف الصحي، ولهذا السبب فإن قدرة البلازما الباردة على أكسدة المواد هي عامل مهم يجب دراسته. في هذه الدراسة تم التحقق عن قابلية البلازما الباردة الناتجة عن تفريغ حاجز العزل الكهربائي (DBD) على أكسدة المواد من خلال استخدام أوقات تعريض مختلفة (5, 10, 15, 20 دقيقة) واثباتها من خلال عدة قياسات: تغير لون الصبغة القرمزي النيلي من اللون الازرق الداكن تدريجيا إلى الأصفر مع تغير ازمان التعريض، الانخفاض الكبير في الاس الهيدروجيني مما يدل على حامضية الوسط بسبب الاكسدة، والزيادة في جهد الأكسدة (ORP) والتوصيلية الكهربائية (EC)، تم إثبات ذلك طيفيًا من خلال لوحظ وجود العديد من أنواع الأكسجين والنيتروجين التفاعلية عند تفاعل بلازما الطور الغازي وبخار الماء بتعزيزه (الأنواع التفاعلية المثارة، والطاقات والالكترونات الناتجة من التفاعل) . وقد لوحظ أن مدة التعرض البالغة 15 دقيقة هي أقصى فترة تحدث فيها الأكسدة وبعدها يحدث التشبع حيث بقي اللون الأصفر لم يتغير وكذلك بالنسبة للطيف.

الكلمات المفتاحية: تفريغ حاجز العزل الكهربائي، إزالة اللون، التوصيلية الكهربائية، صبغة النيلة القرمزية، الاكسدة.