

**Chapter 5 The behavior of the pigment discoloration Permalon Rhodamine B 400% red in a liquid medium after exposure to a non-thermal plasma of different electrical power at atmospheric pressure**

**Capítulo 5 Comportamiento de la decoloración del pigmento Permalon Rhodamine B 400% red en medio líquido, tras su exposición ante un plasma no térmico de diferente potencia eléctrica a presión atmosférica**

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## Abstract

The behavior of the discoloration of the pigment Permalon Rhodamine B 400% red in a liquid medium (120 mg/L) derived from exposure to a non-thermal air plasma at atmospheric pressure was quantified experimentally. Observed changes in dilution were measured as a function of plasma generation electrical power (40.0 W, 60.0 W, 80.0 W, and 100.0 W), as well as exposure time (150 minutes per power). Solution-generated effects were monitored by UV/VIS spectrophotometry measurements (absorbance;  $\lambda = 533$  nm), pH, and temperature change. The absorbance of the solution increased at the beginning of the treatments to decrease after a particular time (15 minutes). The maximum effect was observed at 100.0 W (maximum power used) at minute 150; it decreased by about 2% (maximum decrease at higher power), pH by 43%, and temperature increased from 27 to 58 °C. The results showed that the change in the discoloration of the pigment in a liquid medium directly depends on the working electrical power of the plasma and the exposure time to the treatment of the solution.

## Absorbance, pH, Non-thermal plasma, Water treatment

### Resumen

Se cuantificó experimentalmente el comportamiento de la decoloración del pigmento Permalon Rhodamine B 400% red en medio líquido (120 mg/L) derivado de la exposición ante un plasma no térmico de aire a presión atmosférica. Se midieron los cambios observados en la dilución como función de la potencia eléctrica de generación del plasma (40.0 W, 60.0 W, 80.0 W y 100.0 W), así como del tiempo de exposición (150 minutos por potencia). Los efectos generados en la solución se monitorearon mediante medidas de espectrofotometría UV / VIS (absorbancia;  $\lambda = 533$  nm), pH y cambio de temperatura. La absorbancia de la solución incrementó al inicio de los tratamientos para después de cierto tiempo (15 minutos) disminuir. El máximo efecto se observó a 100.0 W (máxima potencia utilizada) al minuto 150, disminuyó cerca de un 2 % (máximo decremento a mayor potencia), el pH un 43 % y la temperatura incrementó de 27 a 58 °C. Los resultados mostraron que el cambio en la decoloración del pigmento en medio líquido depende directamente de la potencia eléctrica de trabajo del plasma y del tiempo de exposición al tratamiento de la solución.

## Absorbancia, pH, Plasma no térmico, Tratamiento de aguas

### 1. Introduction

At present, the deterioration of water quality together with the problems of depletion of water supplies are one of the many problems faced by modern society in obtaining and using uncontaminated water. In particular, this situation is aggravated by the fact that wastewater is not fully restored in terms of pollution and thus becomes yet another source of contaminants of various kinds; such as microorganisms, bacteria, pesticides, lubricants, synthetic fertilizers, as well as synthetic dyes (Sharma *et al.*, 2022; Goscianska *et al.*, 2015; Yagub *et al.*, 2014; Zhao *et al.*, 2013).

Specifically, synthetic dyes have an increasing percentage of use within the cosmetics, paper, textile, food and fur industries among several others, so their use generates an increase in the volume of wastewater from these industries (Varjani *et al.*, 2020). It is known that the presence of certain concentrations of dyes in water bodies interferes with the biological cycles within them, as it destroys the original ecosystem due to its toxicity and lack of degradability, which represents a serious problem for the health of people, but mainly for aquatic life (Forgacs *et al.*, 2004).

In particular, Rhodamine B dye is one of the dyes that is used in multiple industries and therefore is made with high frequency. It is used in the textile industry, in the manufacture of pens, paints, dyes, explosives, carbon sheets, stamp inks and even in the manufacture of cookies (Hamdaoui, 2011; Imam and Babamale, 2020).

It should be noted that Rhodamine B is one of the most toxic dyes present in textile wastewater due to its high stability and non-biodegradability. Likewise, its high staining capacity is a characteristic that makes it harmful in bodies of water, as it prevents the passage of light and inhibits the bioprocesses of aquatic plants and microorganisms that cohabit there (Sharma *et al.*, 2022).

On the other hand, Rhodamine B has shown fluorescence emission bands under certain conditions, and in its pure state forms highly fluorescent H-aggregates in glycerol, ethylene glycol, methanol and butanol under ambient conditions. The pH-dependent absorption and emission spectra for a fixed concentration of Rhodamine B in the solvents reveal a red shift in the respective absorption and emission maxima (Radiul *et al.*, 2022). This last characteristic is an important factor to consider in the treatments used to decrease the absorbance of Rhodamine B.

From this perspective, the objective of the present experimental study is to observe the effect on the change in absorbance of a solution of Permalon Rhodamine B 400% network in liquid medium, as well as the pH and temperature after exposure for a specific time to an air plasma of different electrical power at atmospheric pressure.

It is known that air plasmas at atmospheric pressure have the ability to generate various molecules (e.g., ozone or H<sub>2</sub>O<sub>2</sub>), as well as multiple species (charged particles) that when reacting with water produce -OH radicals, OH<sup>+</sup> ion, atomic hydrogen and atomic oxygen radicals, which can contribute to the degradation of the compounds in it discharged (Panda and Mathews, 2014).

Knowing and understanding the behavior of the change in absorbance or decrease in the coloration of the solution of interest through this research, gives a guideline to establish a methodology that contributes to the treatment of industrial wastewater with similar characteristics, using an air plasma at atmospheric pressure.

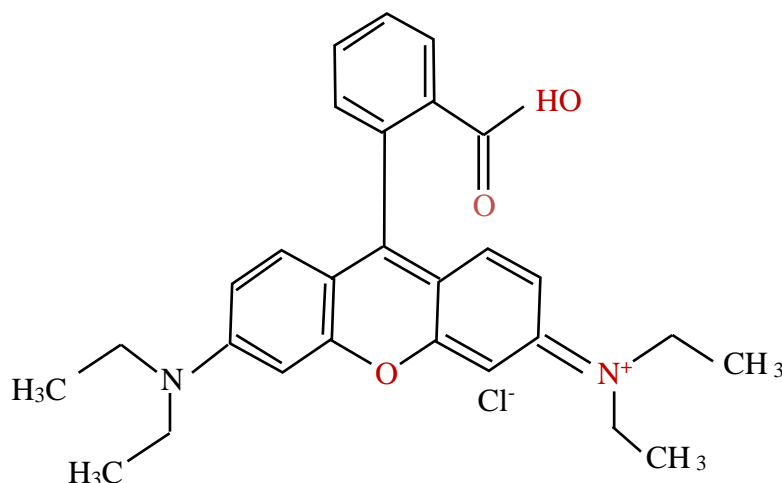
The methodology section presents the chemical characteristics of the dye under study, as well as the techniques chosen to determine the variables of interest according to the experimental device used. The results section shows the graphs of absorbance, pH and temperature change of the solution obtained after the experimentation; from which the most relevant observations are presented in the conclusions section.

## 2. Experimental Methodology

### Rhodmin B Pigment

Rhodamine B pigment (CI 45170) was used without any purification, physical or chemical changes. Its formula and molecular weight are C<sub>28</sub>H<sub>31</sub>ClN<sub>2</sub>O<sub>3</sub> and 479.01 g/mol respectively. All experiments were started with a dye stock solution of 120 mg/L (Rhodamine B in distilled water). Such concentration value was considered in response of the resolution of absorbance measurements obtained by the spectrophotometer used. Higher concentration did not allow clarity at the absorbance maximum. The chemical structure of the pigment is shown in Fig. 2.1.

**Figure 2.1** Chemical structure of *Rhodamine B*

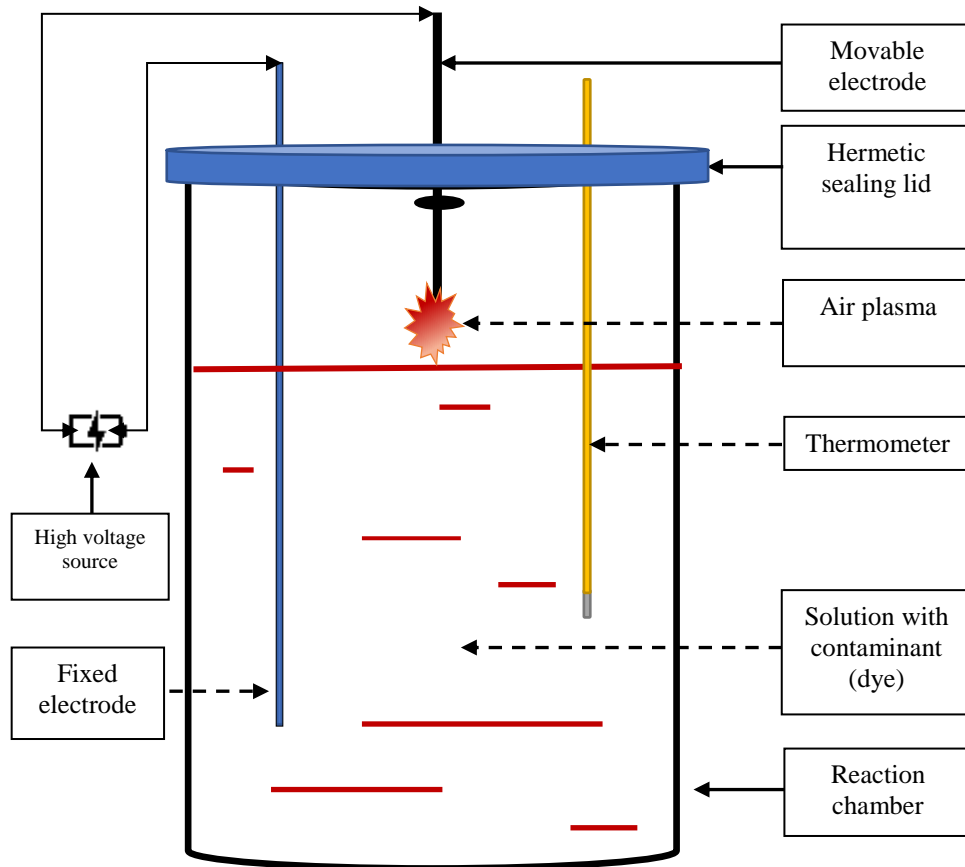


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## Experimental System

The experimental system is similar to the one used in our previous works (Alarcón *et al.*, 2019; Alarcón *et al.*, 2022a; Alarcón *et al.* 2022b; Alarcón *et al.* 2022c). A schematic of this is shown in Figure 2.2. It is basically composed of the following parts: hermetically sealed glass chamber with a capacity of 1.0 L, two tungsten electrodes, a mercury thermometer, and a high voltage source. In this device, one electrode is always immersed in the solution of interest, while the other one is adjusted at a distance of about 2 mm so that the plasma is generated. In particular, the plasma is formed at the interface of the air contained inside the reaction chamber and the solution of interest, as shown in the schematic. The thermometer is always immersed in the solution and can measure the temperature at all times.

**Figure 2.2** Schematic of the experimental setup



*Source of Reference: Own Image*

To subject the solution to plasma treatments, the following process is performed: 500 ml of the solution at a concentration of 120 mg/L are deposited in the reaction chamber of the experimental device used, the plasma generation parameters (voltage and current) are set on the high voltage source (SPELLMAN SL600), the moving electrode is adjusted and then the non-thermal plasma is generated. In particular, four plasma treatments of different electrical powers were considered at an initial temperature of 27 °C; the final temperature depends on the plasma power. Table 2.1 shows the parameters used for each treatment. Four replicates were performed for each treatment. The results presented are the average value of the measurements taken.

**Table 1.1** Parameters considered for this experiment

Treatment	Exposure time (minutes)	Concentration (mg/L)	Electrical power (W)
T1	150	120	40
T2	150	120	60
T3	150	120	80
T4	150	120	100

Parameters considered for the performance of the experiments. Volume of solution used: 500 ml.

## Sampling and measurement of parameters of interest

The process of sampling and measurement of the parameters considered was carried out every 15 minutes once the exposure of the solution to the treatment had begun. For this, the plasma generation is stopped, the temperature reading is taken (thermometer of the experimental system) and a sample is extracted to measure the absorbance and pH (Hach DR 3900 spectrophotometer and HI 9813-6N potentiometer, respectively). Once the necessary measurements have been taken, the sample solution is added to the reaction chamber and the treatment is resumed. This process is repeated until the experiment has lasted 150 minutes.

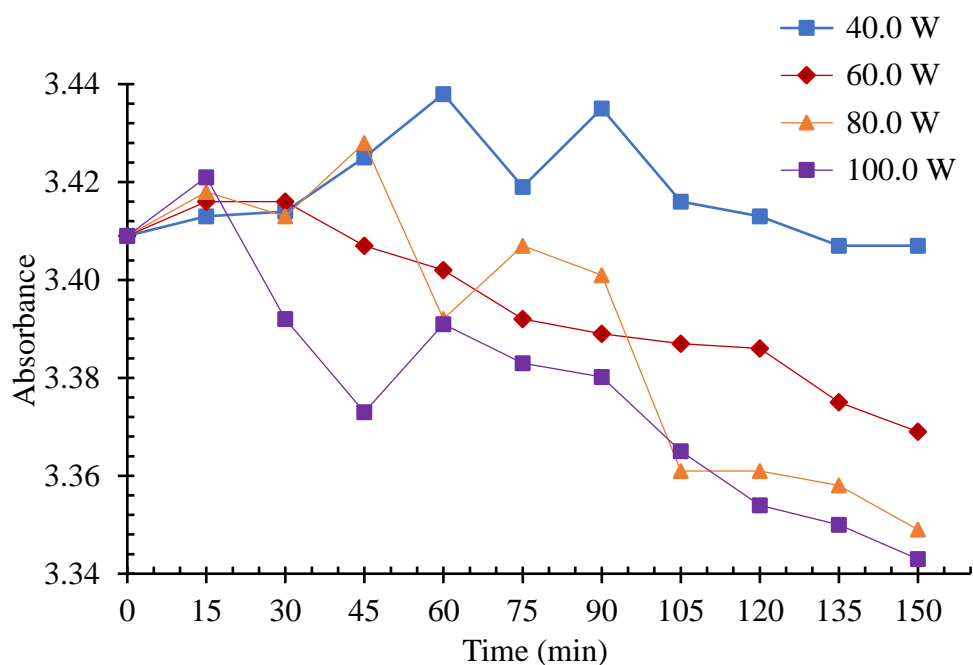
## 3. Results and Discussion

Given the fluorescence characteristics of the Permalon Rhodamine B 400% network dye under certain conditions, in this study the changes of the absorbance value were measured when a solution of this dye is exposed to an air plasma of different electrical power at atmospheric pressure, as well as the change of the pH value and the temperature of the solution.

### Absorbance

The absorbance values of the solution of interest show a particular behavior very different from that of other dyes under the same conditions and treatments. Graph 3.1 illustrates such behavior as a function of exposure time to air plasma treatments at atmospheric pressure and for different values of plasma generation power.

**Graph 3.1** Change in absorbance.



*Source of Reference: Own Image*

It is observed that the absorbance for the first fifteen minutes of treatment increases its value with respect to the initial value (3.409). Such behavior is presented for the four plasma treatments and shows an increasing dependence on the electrical power used (40, 60, 80, and 100 W), that is, the higher the plasma generation power, the greater the increase in the absorbance value (3.413, 3.416, 3.418 and 3.421) respectively.

On the other hand, for the 40 W electrical power treatment, the absorbance continued to increase (not so for the other treatments) until reaching a value of 3.438, corresponding to the exposure time of 60 minutes. After this time, the absorbance decreases to a value of 3.407.

That the increase in absorbance for the first fifteen minutes of exposure for all plasma treatments is proportional to the plasma generation power and that the increase in absorbance value is maintained for 60 minutes for plasma generated at the lowest power (40 W), may have a response in the characteristic fluorescence of the Rhodamine B dye.

In a recent experimental study (Radiul *et al.*, 2023), a previously undetected Rhodamine B fluorescence emission band was found, which is located between the spectral wavelength of 675 nm to 717 nm for the following solvents at ambient conditions: glycerol, ethylene glycol, methanol and butanol. Such a band is suggested, could be associated with the H-aggregates (H-dimer) of Rhodamine B and is confirmed by a blue-shifted band at 515 nm in the absorption spectra of Rhodamine B, in all solvents. In the present case, the absorbance maximum was presented at  $\lambda = 533$  nm; which can be explained in terms of the working concentration (120 mg/L) (Radiul *et al.*, 2022). On the other hand, the formation of fluorescent H-aggregates was further corroborated by the variation of absorption and fluorescence peak intensity dependent on the experimental working concentration and pH. In particular, pH-dependent absorption and emission spectra for a fixed concentration of Rhodamine B in solvents reveal a red shift in the respective absorption and emission maxima (Radiul *et al.*, 2023).

For the other treatments (60, 80 and 100 W), the absorbance generally showed a decreasing behavior, reaching values of 3.369, 3.349 and 3.343 respectively at 150 minutes of plasma exposure. The largest decrease was observed for the 100 W treatment, decreasing a value of 0.066, equivalent to almost 2 %. It is noteworthy that the decrease in the absorbance value of the solution at 150 minutes of exposure to plasma is related to the power of plasma generation, the higher the power of plasma generation, the greater the discoloration.

## pH.

The solution changes pH (decreases) as it is exposed to the plasma. The rate of decrease is associated with the plasma generation power and with the exposure time. The higher the plasma generation power, the faster the pH values decrease, the longer the exposure time to the plasma, the higher the acidity of the solution. Graph 3.2 shows this behavior.

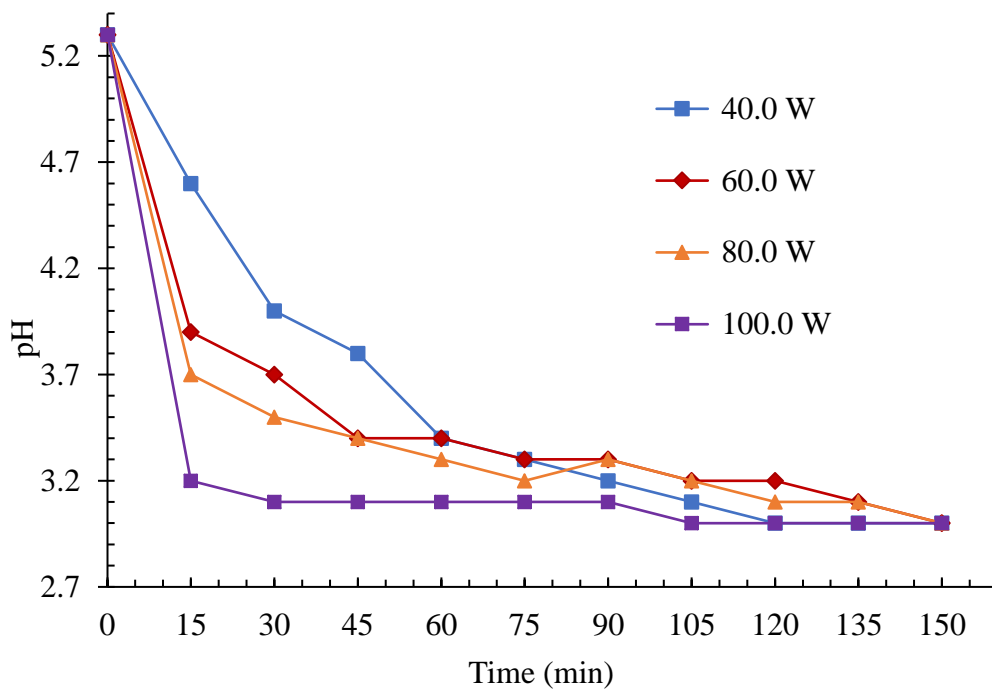
In all the experiments, a rapid decrease in pH can be observed during the first 15 minutes, after which the decrease is slow and gradual until reaching the minimum value reached.

The pH values observed after 150 minutes of treatment changed from 5.3 to 3.0 (equivalent to 43 %) for all treatments, only that some treatments reached it in less time than others. Similar results regarding the behavior were obtained for other dyes exposed to plasmas under similar conditions (Alarcón *et al.*, 2019; Alarcón *et al.*, 2022a; Alarcón *et al.* 2022b; Alarcón *et al.* 2022c).

The decrease in pH is attributed to the chemical reactions that occur during the application of the plasma. On the one hand and considering the configuration of the experimental system, there is the generation of hydronium ions, obtained from the interaction of CO<sub>2</sub>, water and plasma, and the subsequent reactions. Reactions (1) - (3).



On the other hand, in the reactor chamber and due to the generation of compounds such as HNO<sub>3</sub>, HNO<sub>2</sub>, among other products that can be formed in moist air plasmas, there is a change in the pH of the solution (Fahmy *et al.*, 2018; Shimizu *et al.*, 2020; Alarcón *et al.*, 2022a; Safenraider *et al.*, 2020).

**Graph 3.2** pH change of the solution as a function of exposure time and plasma generation power

Source of Reference: Own Image

It should be considered that the change in pH of the solution after being exposed to the plasma is a consequence of the treatment, however; it also contributes to the change in the absorbance value and the wavelength at which it is determined (Radiul *et al.*, 2023).

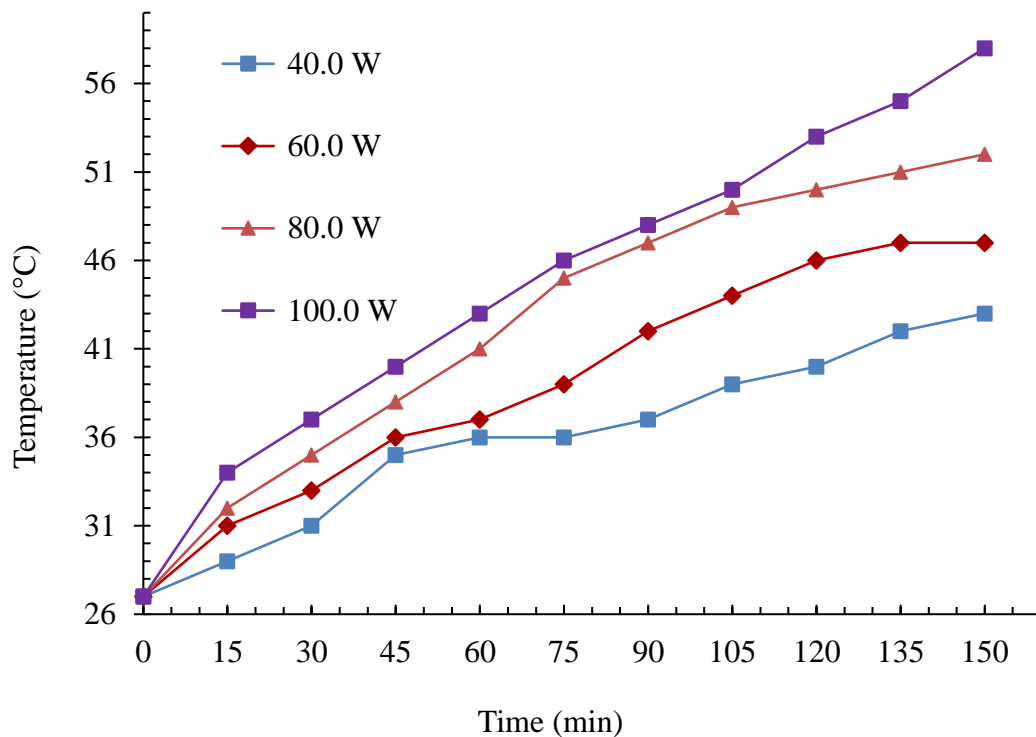
### Temperature

Graph 3.3 shows the behavior of the temperature change of the solution as a function of exposure time and plasma generation power. It is observed that as the exposure time increases, the temperature value also increases. A similar behavior is shown for all plasma generation powers (40, 60, 80 and 100 W), in particular; the temperature changes from an initial value of 27 °C to 43, 47, 52 and 58 °C respectively.

Given the volumes of solution treated and the plasma generation powers, the rate of temperature change is different for each treatment. As the energy provided to the system increases, the rate of temperature rise increases as well. It is noteworthy that the temperature rise is not linear; it could be associated with a degree 2 polynomial behavior.

In particular, the temperature increase of the solution presents mainly two physical processes, the first one of heating of the solution with little evaporation and the second one of heating and at the same time greater evaporation (Alarcón *et al.*, 2022a).

It has been observed that increasing temperature does not necessarily generate changes in the discoloration of a dye solution (Alarcón *et al.*, 2022b), however, it is necessary to perform the experiments for the solution of interest in the considered temperature range.

**Graph 3.3** Solution temperature change behavior

*Source of Reference: Own Image*

#### 4. Acknowledgements

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#### 5. Conclusions

The discoloration behavior of the Permalon Rhodamine B 400% network pigment in liquid medium was quantified after its exposure to a non-thermal plasma of different electrical power (40, 60, 80 and 100 W) at atmospheric pressure and with a duration of 150 minutes per treatment. The change in pH and temperature values was also determined.

The absorbance of the solution showed for all the treatments, a singular behavior of increase for the first 15 minutes of exposure to the plasma, this; due to the fluorescence characteristics of Rhodamine B. The minimum absorbance value reached for the solution was almost 2 %; it rises and then decreases. The higher the plasma generation power, the greater the decrease in the absorbance value and pH. The higher the temperature increase.

An air plasma with the characteristics of the one used in the present investigation, stimulates and enhances the fluorescence characteristics of the Rhodamine B.

#### Research suggestion

The present investigation showed an increase in absorbance of the solution of interest in the first 15 minutes of treatment (first measurement) and then a decrease (second measurement). It is considered to take measurements of absorbance and other variables at shorter intervals (1 minute), to analyze the behavior in a more detailed way and to determine the fluorescence.

The implementation of the same experiments at intervals of 20 minutes is also considered, with a longer exposure time (300 minutes) to know if the absorbance continues to decrease.



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