



# PRINTED ELECTROCHEMICAL UV SENSOR

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Chemical Engineering. Final degree project.

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## Abstract

The molecules of titanium dioxide ( $\text{TiO}_2$ ) have the capacity be excited by means of ultraviolet light of high energy, for that is a great semiconductor with photocatalytic properties. Thanks to emulsifier, the  $\text{TiO}_2$  can be printed on carbon electrodes, in a substrate of polymer (PET). The distance between the drops of  $\text{TiO}_2$  or the number of layers of the screen printing electrodes, with others conditions, could be varied to see the characteristics of the sensors.

The samples were treated with ultraviolet light, previous treatment before the photocurrent measurements, and during the measurements of it. The  $\text{TiO}_2$  printings on the screen printed carbon electrodes was applied to build photoelectric sensors, by it were obtained responses of stable and sensitive photocurrents.

Key words: Inks, electrodes, sensors, screen printing, electrochemical, ultraviolet light, photocurrent, drops distance, dioxide of titanium.

## Resumen

Las moléculas de dióxido de titanio ( $\text{TiO}_2$ ) tienen la capacidad de ser excitadas por medio de la luz ultravioleta de alta energía, por ello, es un buen semiconductor con propiedades fotocatalíticas. Gracias a un emulsionante, el  $\text{TiO}_2$  puede ser impreso en electrodos de carbono sobre un substrato de polímero (PET). La distancia entre las gotas de  $\text{TiO}_2$  o el número de capas de los electrodos impresos, con otras condiciones, podría ser variado para ver las características de los sensores.

Las muestras fueron tratadas con luz ultravioleta, tratadas previamente antes de la medición de la fotocorriente y durante las medidas de ellas. Las impresiones de  $\text{TiO}_2$  sobre electrodos serigrafiados fue aplicado para construir sensores fotoeléctricos, por ello fueron obtenidas respuestas de fotocorrientes estables y sensibles.

Palabras clave: Tintas, electrodos, sensores, serigrafía, electroquímica, luz ultravioleta, fotocorriente, distancia de las gotas, dióxido de titanio.

## Abstrakt

Molekuly oxidu titaničitého (TiO<sub>2</sub>) mohou být excitovány ultrafialovým zářením o vysoké energii, proto je oxid titaničitý dobrým polovodičem s fotokatalytickými vlastnostmi. Díky emulgátoru může být TiO<sub>2</sub> na polymerním substrátu (PET) tisknut na uhlíkové elektrody. Pro charakterizaci senzorů může být vzdálenost mezi kapkami TiO<sub>2</sub> nebo počtem vrstev tištěných elektrod s jinými podmínkami měněna.

Vzorky byly před i během měření ozařovány ultrafialovým zářením. Tisknutý TiO<sub>2</sub> na uhlíkových elektrodách byl použit k sestavení fotoelektrických senzorů, čímž byly získány stabilní a citlivé fotočlánky.

Klíčová slova: inkousty, elektrody, snímače, sítotisk, elektrochemie, ultrafialové záření, fotočlánky, vzdálenost kapek, oxid titaničitý.

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## 1. INTRODUCTION

Inside of the necessity surged for technologic advances and recent discoveries, electrochemical sensors are in expansion process and integration in different models and systems. This sensors can realize a lot of very assortment functions, from monitoring of the contamination on a environment until detecting some radiations, or in health ambits.

During the progress of the study, we are going to see different ways of do sensors, their tests in some conditions, conductivity and knowledge of their components.

The objective of this work consist in the study of the characteristics of design of the electrodes to get the better sensible ultraviolet light sensors and then it can be used on equipment or machines.

## 2. MATERIAL, EQUIPMENT AND SOFTWARE

The sensors were fabricated with an universal screen printing machine SD 05 for flat printing (Roku Print, Germany).

The inks used were:

- Carbon Loctite EDAG PF 407C (Henkel, Netherlands).
- TiO<sub>2</sub> Aeroxide P25 (Sigma-Aldrich, Czech Republic).

Dowanol PM, Propylene glycol methyl ether (Sigma-Aldrich, Czech Republic).

The substrate used was:

- PET (polyethylene terephthalate), 150µm (Fatra, Czech Republic).

The electrolyte used was HClO<sub>4</sub> (perchloric acid), (Sigma-Aldrich, Czech Republic). This electrolyte was diluted with distillate water until get a dissolution 0.1M. Also, it was added on the electrolyte Glycerol (Sigma-Aldrich, Czech Republic) in various concentrations.

The printing of the TiO<sub>2</sub> on the electrode was realized with the inkjet printer machine Dimatix DMP-2850 (Fujifilm, USA).

The samples were treated with a Hg lamp of ultraviolet light, 250W (Ultra Light, Liechtenstein).

The electrochemical measures were realized with a potentiostat (National Instruments, Czech Republic) with two modules, one of data entrance for the current and another for the voltage exit:

- C Series Universal Analog Input Module, NI 9219 for the current.
- C Series voltage Output Module, NI 9263 for the voltage.

This potentiostat was connected and controlled on a LabView software (National Instruments, USA).

The photocurrent was measured with a Hg lamp of ultraviolet light (Ultra Light, Liechtenstein).

### **3. THEORETICAL FUNDAMENTS**

#### **3.1. Theoretical antecedent**

In this work we are going to explain and study the screen printing interdigital sensors, their production, uses and advantages.

To begin with, we must define chemical sensors and the electrochemical sensors. They are chemical devices which respond to changes in the potential or in the electric current for the presence of elements or compounds in the means where they are and which they interact with. The chemical sensors receive that definition because they are constituted for a chemical element, organic or inorganic. For that, the chemical sensors are very selective depending on the element which is fabricated.

The electrochemical sensors are constituted for a cell, using two or three electrodes and a means where produce the chemical reaction in the electrode (electrolyte). These sensors are based on which the electrode bases his response on the measurement of an electrical property generated in an electrode system (potential, current, relation of current-potential, etc.).

Depending on the technique of the transducer, the chemical electrodes is divided in three big groups: conductive or capacitive, the potentiometer and the amperometric.

- Conductive or capacitive are based in the measurement of changes of conductivity provoked for the analyte.
- Potentiometer determines a potential difference between a work electrode and one of control.

In the amperometry, the potential is permanent on the work electrode, respect one of reference, being able to fabricate the work electrode of metals or carbon. Also, it has another electrode called auxiliary for complete the electrochemical cell.

Conventional electrochemical sensors presented deficiencies that meant that their use didn't have a not very good durability. Also, the maintenance costs and repaired used be excessively high. So, the relation between the use and the cost make it's necessary the study of others electrodes which can realize the same functions, but with a cost lower.

Inside this study the best, or ones look very convenient, are the screen printing sensors. The screen printing sensors will allow us to perform and improve techniques of analysis putting the electrochemical sensors in first place in the future like the principal sensors for the realization of analysis and control of information on factors in real time. The information which can be analyzed these sensors can come from the state of the environment, the pollution surround it, chemical hazards or information about the health of a person. Also, these electrodes can realize functions of elimination of colorants or other chemical products in a meant with some lightly energy, like the ultraviolet light or the solar light.

The screen printing sensor started around the middle of the 90's decade, for that it is considered a modern technology.

### **3.2. Advantages**

The principle of these sensors, or electrodes, are based in the consideration of the change of the conventional substrate on were impressed. A principle of these sensors is they must be flexible, for that the substrate where will be impressed should be capable of adapt to different conditions of movement and deformation.

The versatility of the fabrication technique of screen printing can make the realization of different geometries, drawing or forms of the electrodes. This is a great advantage for the fabrication because for everyone of the required uses of the sensors and electrodes can design the best. The inks used in these techniques is very varied, with multiples chemical elements, being an advantage because depends the properties which we need on the sensor we can choose the best it. Between them are the carbon, gold or platinum, being able change with additives of others substances to make the electrode more selective on the analysis.

Another advantage on these characteristics of the electrodes is the low cost required for the production of them. This makes the sensor disposable once it doesn't work like it would wait, making also eliminate cleaner works which are on conventional electrochemical sensors.

Another important point about the screen printing sensors, as it's already said, is the substrate. Is not the chemical compost of the electrode the most important thing on the design and the fabrication of the sensor. The substrate must be of a material with the adequate properties for a good work. In the list of materials can be used for these functions we find the polythene, polypropylene, polyamides, Teflon, etc. In our work, we are going to use a substrate of PET (polyethylene terephthalate), a thermoplastic polymer with a high crystallinity grade, property that will help us when we realize the experiments. It has also a high resistance to wear and corrosion, a good chemical and thermal resistance. [1]

We must mention the substrate also of plastic can be of the other material like ceramics, steel or clothing. In the characteristics of the substrate we find the plastic should be transparent, flexible and low cost.

### **3.3. Procedure and parts**

Once see the characteristics of the sensors we are going to concrete on the interdigital screen printing electrodes. These are the electrodes which according to their design are formed for a printing with two tracks for the connection and they are fabricated on a substrate of glass or plastic. It consist in a small target where it's find a integrated circuit which consist in the electrodes per se with electric contacts for their connections on the measurement system.

The process of fabrication of these electrodes consist in a ink deposition on the substrate using a stencil with the desired design or drawing. Then, it is realized an stage of dry or a cured. So it can be cover leaving the connections free for they can be used.

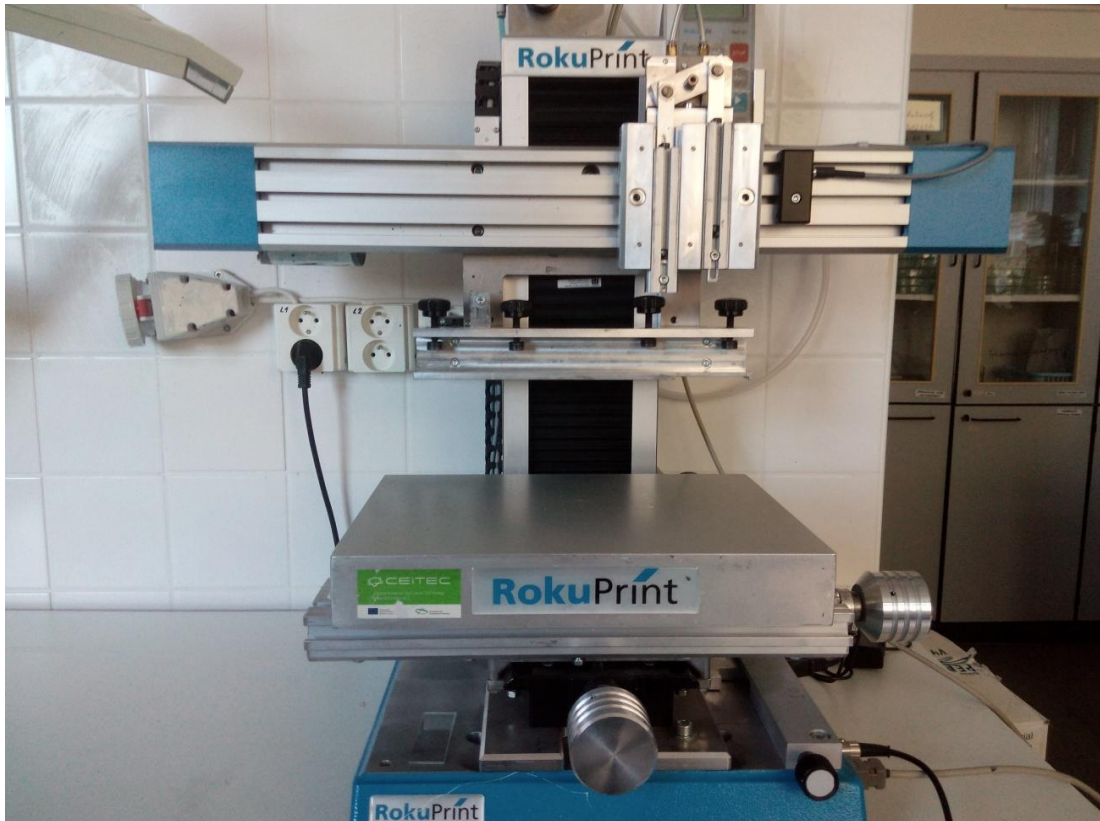
#### **3.3.1. Ink of electrode (carbon)**

Inside on the variety of elements used like inks which we can utilize for impress the electrodes, the carbon is a material really attractive for the construction of these. It's because the low cost of the element as of the really good chemical characterizes presented, with an ample potentials window, the big facility of the electricity conduction and the low background currents. It's a chemically inert material and difficult to chemically modify. But it has the capacity to support on the moment when it's necessary add others chemicals elements, or others composts, which can make the function which it was fabricated.

In this case we will use the carbon for printing EDAG PF407C, a material which is used for printed resistors, membrane touch switches, keyboards, heating elements and flexible circuits and protection against electrostatic discharge. It has characteristics of be a conductive material which is used principally for screen printings, it has a good screen residence time, good adhesion and a flexible low temperature drying cycles.[2]

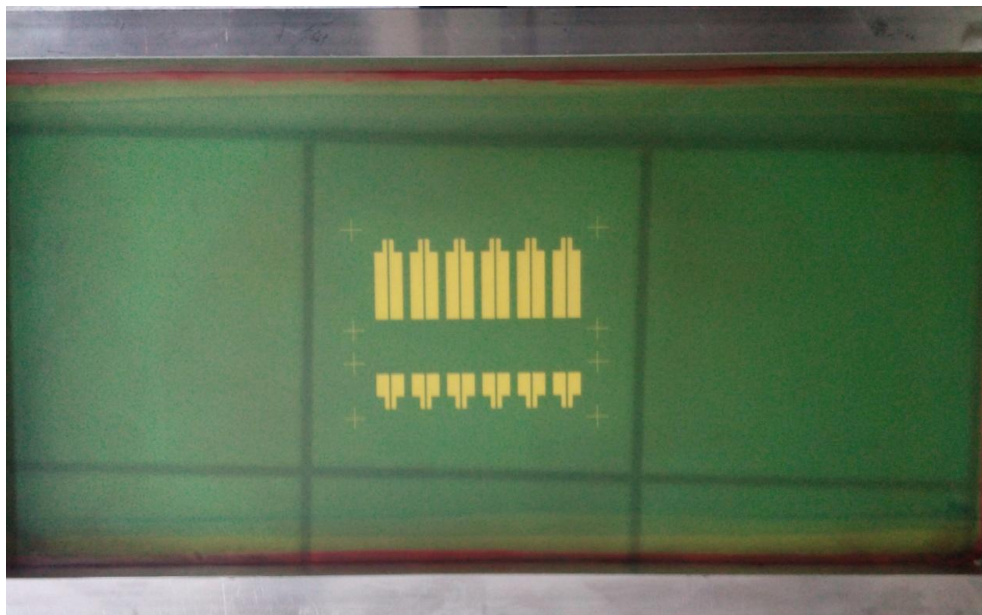
#### **3.3.2. Screen printing machine**

It will use to realize the impress of the electrodes on the substrate an universal screen printing machine SD for flat printing, trademark Roku Print, Germany (**Figure 1**).

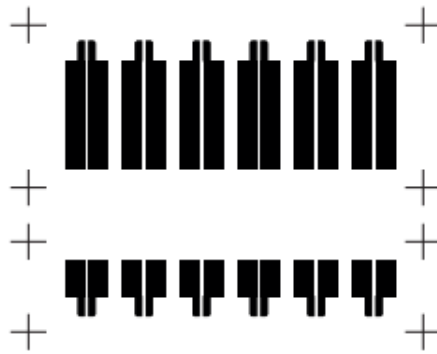


**Figure 1.** Screen printing machine SD for flat printing

With this machine, it is necessary use a support as stencil (**Figure 2**) which it has drawn the design of the electrodes:



**Figure 2.** Stencil of the electrodes

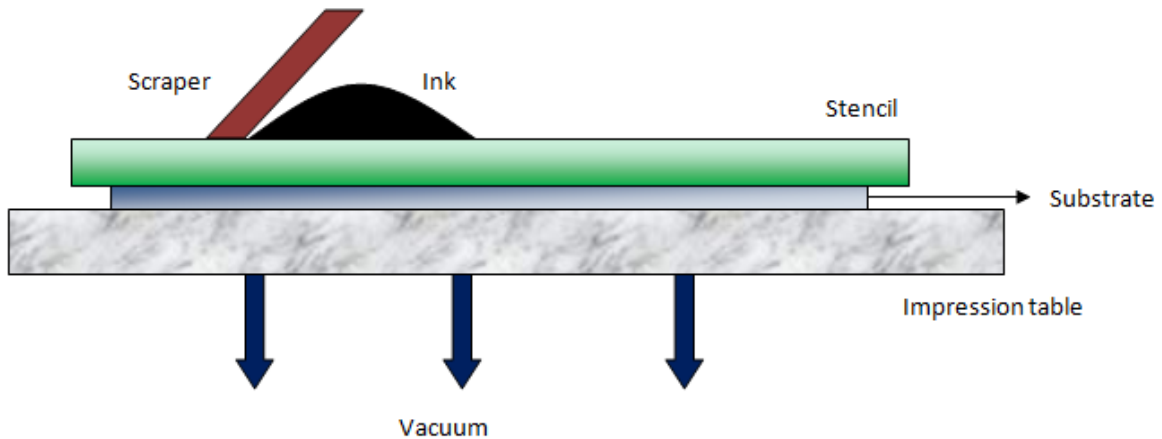


**Figure 3.** *Diagram of the electrodes.*

The **Figure 3** shows a diagram how are going to be the electrodes after the printing.

The screen printing machine has a printing table which support the substrate. On him it's collocated the stencil and is attached on the table. On the stencil is collocated an appropriated amount of the ink used for impress the sensors, in this case, carbon. Once all is prepared the printing is ready. The printing is realized with a scraper and also the screen printing machine has a compressor of air under the impression table, on the substrate, for keep it and it doesn't move during the printing. The first printing won't be good like is waited because the carbon has to extend well. So, it is necessary make some proves of printing before obtain a drawing can be worth, or well, give various printings on the same substrate, but without move it. That's means the electrode will have some layers of carbon for his fabrication, although also it can make the electrode without mistakes at beginning. It's an important fact the number of layers which is going to made the screen printings because depending of the number of layers, the conductivity will be more efficient. As regards more layers have, higher conductivity. But it has a limit because maybe exist a saturation of the carbon. A thickness recommended of printing is between 6 and 10 $\mu$ m. This thickness is like two or three layers. All the electrodes will have these layers.

You have to be very careful in the finalization of one printing because the ink can spread and you have to see the printing has not holes that with a naked eye doesn't see it.

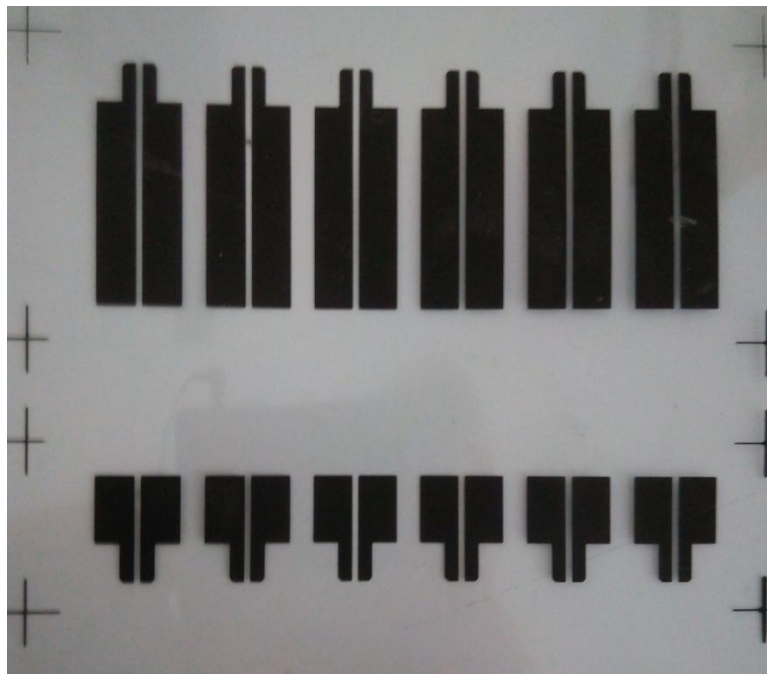


**Figure 4.** *Diagram of the principal screen printing process.*[3]

Once the printing is made it's allowed to dry on ambient air for a few minutes. Allow to dry with the ambient temperature (20-22°C) of the laboratory.

The measurement of the electrodes is 35mm length and 5mm width.

With this method, we obtained 40 transparencies, plastic sheet, with 6 electrodes in everyone. Later, they were cut individually for better using. The next figure (Figure 5) show the electrodes already finished.



**Figure 5.** *Screen printing electrodes on transparent.*

### 3.3.3. TiO<sub>2</sub>

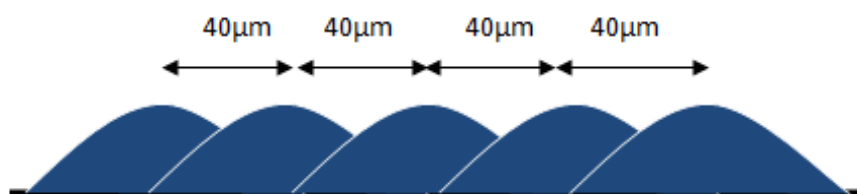
Once the electrodes were dried, they were carried to the inkjet printer machine Dimatix DMP-2850, trademark Fujifilm, for the TiO<sub>2</sub> implantation. Dioxide de titanium



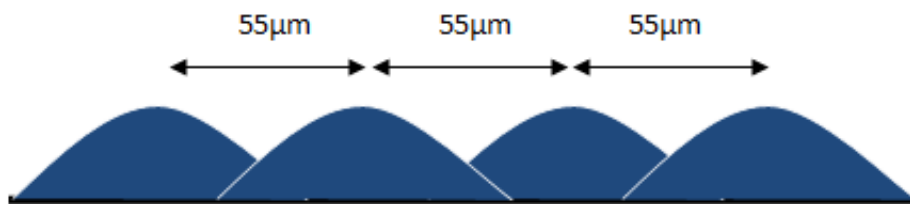
is a semiconductor metallic oxide with photocatalytic properties when is found in ultraviolet light expose ( $\lambda \leq 400\text{nm}$ ). Is the most used semiconductor in photocatalysis because is inert chemically, is not toxic, stable to the photochemical and chemical corrosion, abundant and very economic. Also it poses a energy gap of 3.2eV which can be excited whit ultraviolet light, which can be provide with solar light. In this work is going to utilize always in colloidal suspension which we will attach on a inert support (carbon). We must define the photocatalysis as the electrochemical reaction involve the ultraviolet light absorption and a catalyst like a semiconductor material. During the process it will produce oxidation and reduction reactions. Using dioxide of titanium as catalyst we realize a reaction where it is produced hydroxyl radicals  $\cdot\text{OH}$  by means of the activation of the catalyst (ultraviolet light). Then, it happens a electrons promotion of the valence bond to the conduction, it in turn forms a positive space in this valence bond and these interact with the hydroxide ions and water for make the free radical  $\cdot\text{OH}$ . The electrons in the conduction bond interact with the molecular oxygen to make the superoxide radical ( $\cdot\text{O}_2$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) which at the same time, generate  $\cdot\text{OH}$  radicals. The velocity of reaction is proportional to the light intensity. For this, when we applied more ultraviolet light power the reactions will happen faster, and then, it gets a higher number of extracted electrons which implicate higher current. [4]

$\text{TiO}_2$  is found with a emulsifier because the collocation on the electrode is by drops with a cartridge. To get this dissolution of  $\text{TiO}_2$  is, as it has been said, mixed with an emulsifier like the Dowanol PM (1-methoxy-2-propanol) which is an active and tail solvent for solvent based gravure and flexographic printing inks. It is used also for coupling agent in solvent blends for water-based gravure, flexographic, and silk screen printing inks, as a carrier solvent for inks, coupling agent and solvent in cleaners and as a solvent in pesticides. In our case we will utilize for suspend on the  $\text{TiO}_2$  dissolution, doesn't precipitate and to tie it better on the printing.[5]

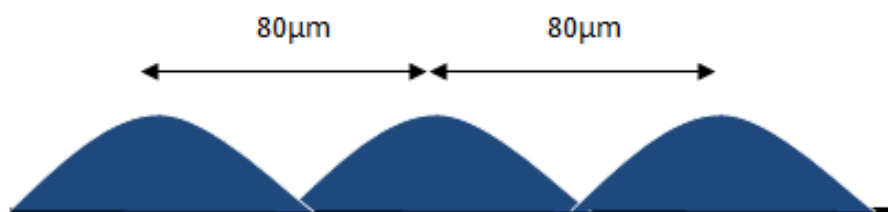
We must adjust the machine by numerical control so the print is exactly on the electrode. Before the printer of the drops of the  $\text{TiO}_2$  on the carbon we have to adjust the distance between every drops.



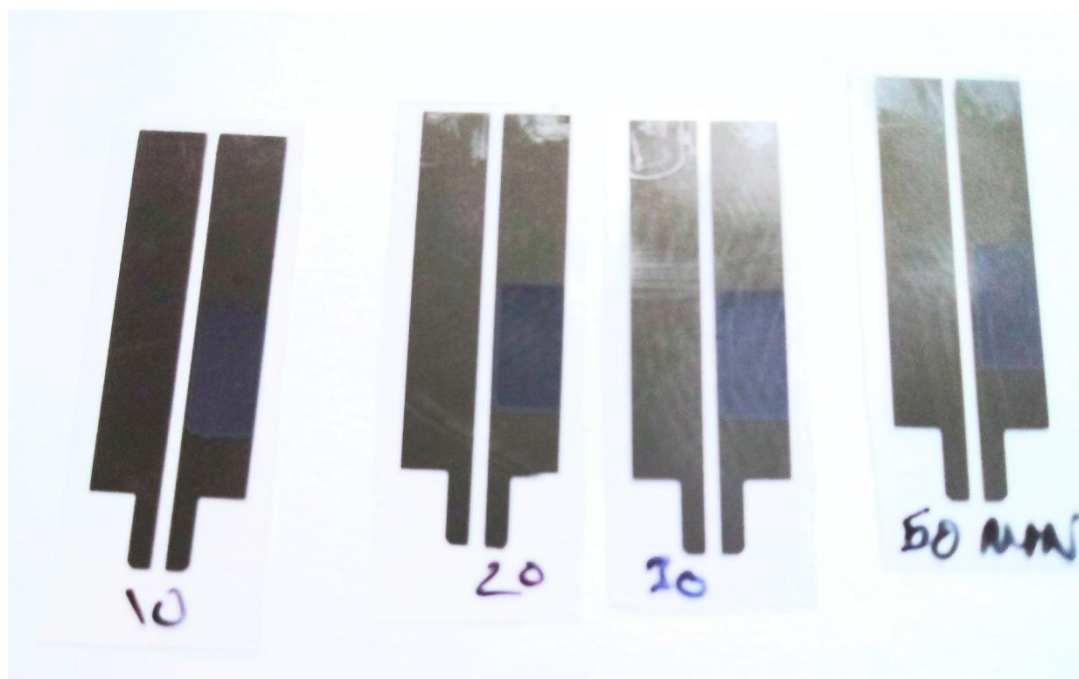
**Figure 6.** Diagram of  $\text{TiO}_2$  droplets on carbon with a distance of  $40\mu\text{m}$ .



**Figure 7.** Diagram of  $\text{TiO}_2$  droplets on carbon with a distance of  $55\mu\text{m}$ .



**Figure 8.** Diagram of  $\text{TiO}_2$  droplets on carbon with a distance of  $80\mu\text{m}$ .



**Figure 9.** Electrodes separated with the  $\text{TiO}_2$  print.

The print of the  $\text{TiO}_2$  is shown a naked eye with a bluish tone on the black carbon (**Figure 9**). Once is printed is collocated the number of his distance between the drops, the number of the sample and, later, the number of the time were under the

ultraviolet lamp (the previous treatment). Then, is allowed dry with the same way, with ambient air in the laboratory a few minutes. The measurement of the ink printing is 10mm length and 5mm width.

After that, it's proceed to realize the previous treatment with a ultraviolet lamp of Hg, trademark Ultra Light with a intensity of 31W/cm and a wavelength of 350nm. Electrodes are placed inside a crystallizer on a millimeters of distillate water, or under them, for prevent the heat and the time that is under the light is timed. This is realized to get the intercrossing of the molecules of  $\text{TiO}_2$  between them, provoking a higher conductivity of the electricity when the ultraviolet light is exposed.

After this procedure, we can start to realize the measurement. Firstly, the preparation of the electrolyte where we will put the electrodes for the amperometries. Electrons alone cannot normally pass through the electrolyte; instead, the chemical reaction happens at the cathode, consuming the cathode electrons, and another reaction occurs at the anode, producing electrons to be captured by the anode. As a result, a cloud of negative charge develops in the electrolyte around the cathode, and a positive charge develops around the anode. The ions in the electrolyte move to neutralize these charges so that the reactions can continue and the electrons can continue to flow. The electrolyte is a dissolution of perchloric acid ( $\text{HClO}_4$ ) 0.1M. The value of his conductivity is  $37\mu\text{S}/\text{cm}$ . It will added in a glass bucket of 40mL for the measuring.

We have to mention the needing of the polarization of the electrodes. The emission of electrons has a low quantum efficiency on the photocatalytic degradation. To get more efficiency (separate more electrons) is applied electricity (electric polarization) which is possible thanks to the carbon substrate. For this, the polarization of the electrodes is necessary for the realization of measuring of the current and voltage on the electrodes, doing the positive pole (anode, where the oxidation reaction happens) be the part of the electrode with the  $\text{TiO}_2$  ink, and the negative pole (cathode, where the reduction reaction happens) the part without ink. When an electrode is placed in an electrolyte and a voltage is applied, the electrolyte will conduct electricity.

It is connected on a potentiostat, trademark National Instrument, with two modules, one of data entrance for the current and another for the voltage exit. The potentiostat is in turn connected on a computer which is in charge of the data register through a LabView program.

In front of the cuvette it will collocated a conventional ultraviolet lamp to realize the measuring and check how reaction the electrodes when the ultraviolet light is exposed. The ultraviolet lamp has a wavelength of 350nm, and the intensity at beginning is the  $0.9\text{mW}/\text{cm}$ . But, the lamp has the capacity of move closer and move

## Printed electrochemical UV sensors

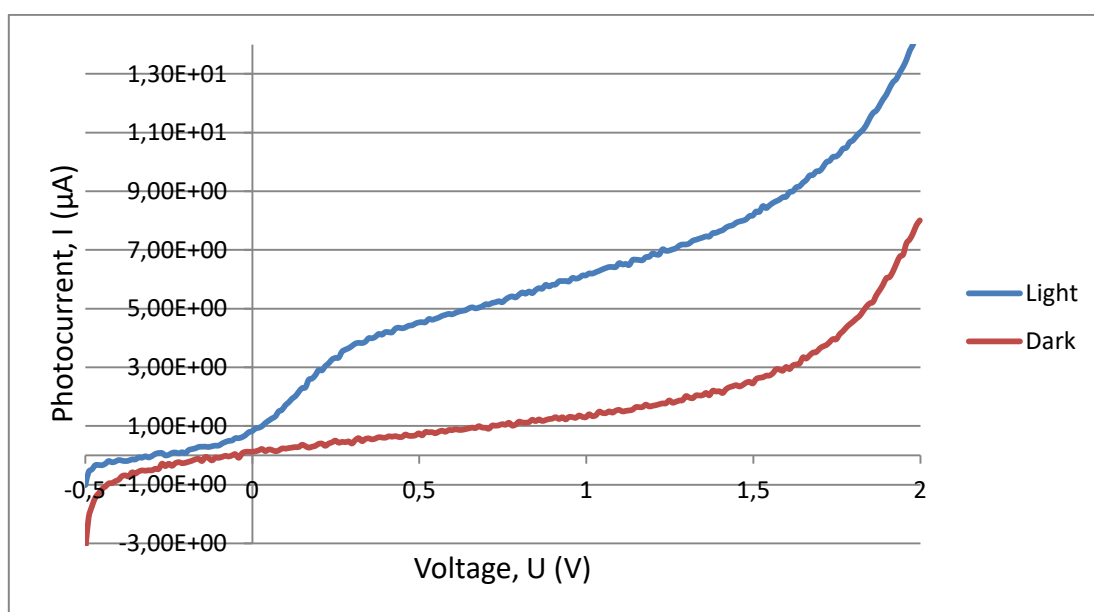
away, So, when we want more intensity, or less, we could move closer or move away the lamp to get the desired intensity. The intensity was measured with a conventional radiometer.

## 4. EXPERIMENTAL PART

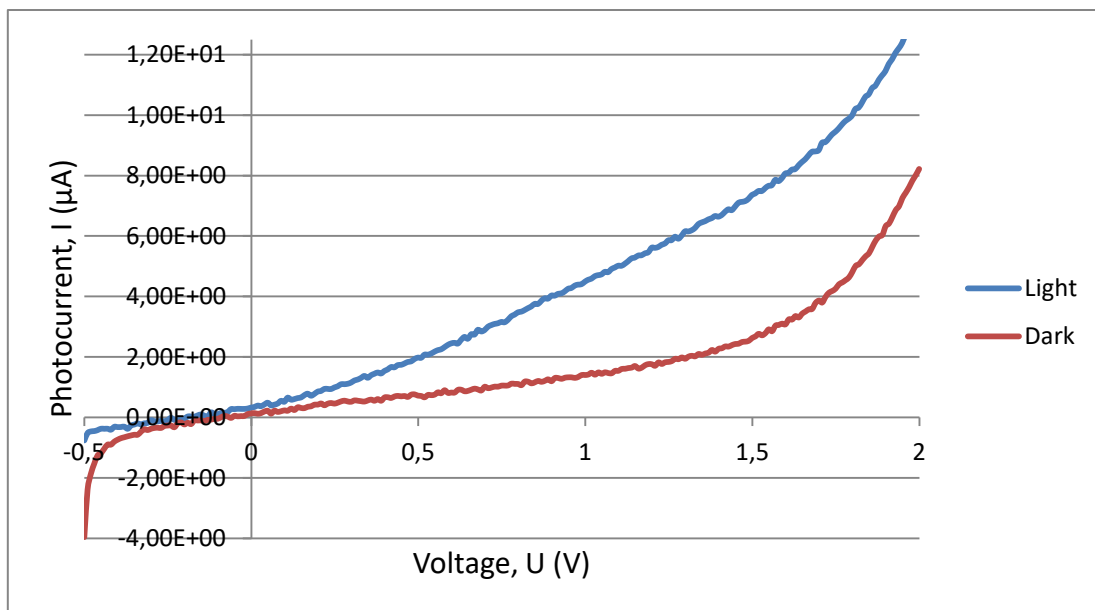
### 4.1. Process check

#### 4.1.1. Evolution of current in front the voltage with a UV light exposure and without it

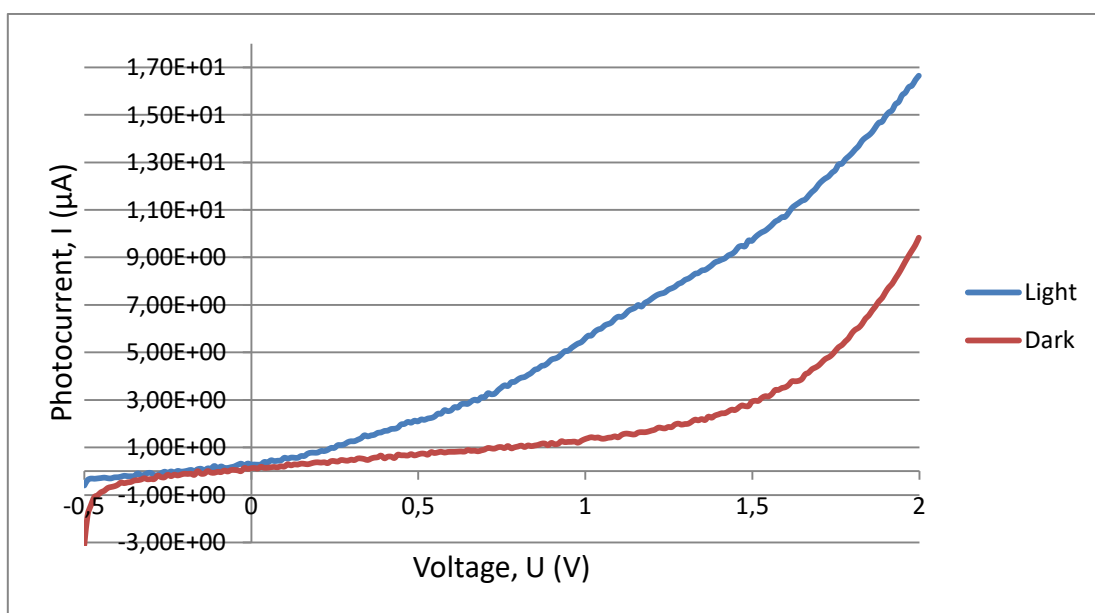
We start using the electrodes. It is applied a potential difference of -0.5 to 2V, with 10 mV of interval, while it is applied ultraviolet light to see the evolution of the intensity in function of the voltage. It is compared the same result with the same conditions, but without the ultraviolet light.



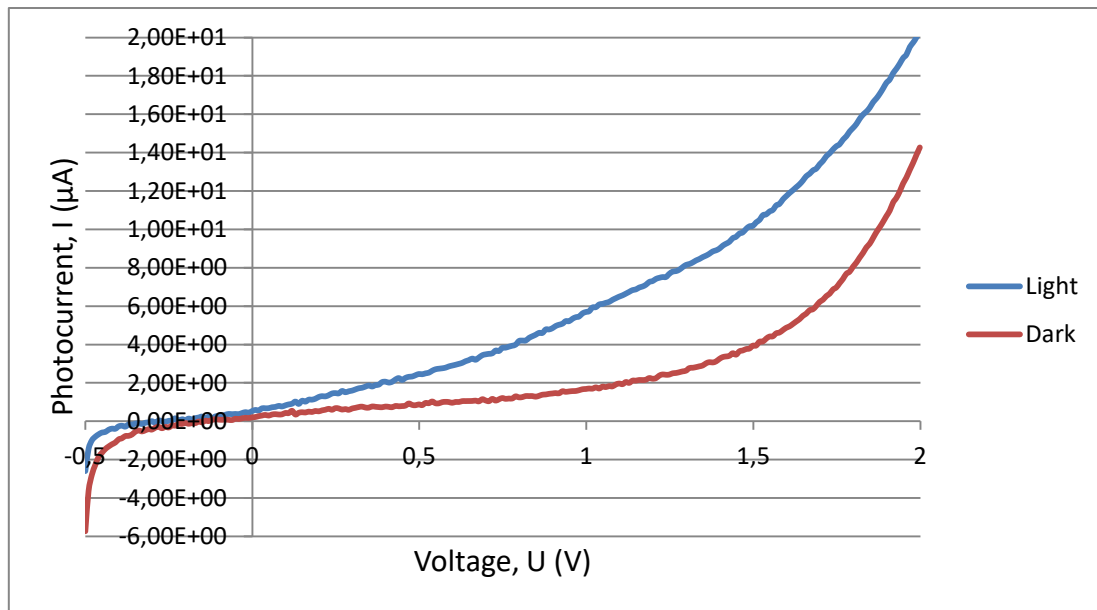
**Figure 10.** *U front I between exposure ultraviolet and without it (0 min of previous treatment).*



**Figure 11.** Compare U front I between exposure ultraviolet and without it (10 min of previous treatment).



**Figure 12.** Compare U front I between exposure ultraviolet and without it (20 min of previous treatment).

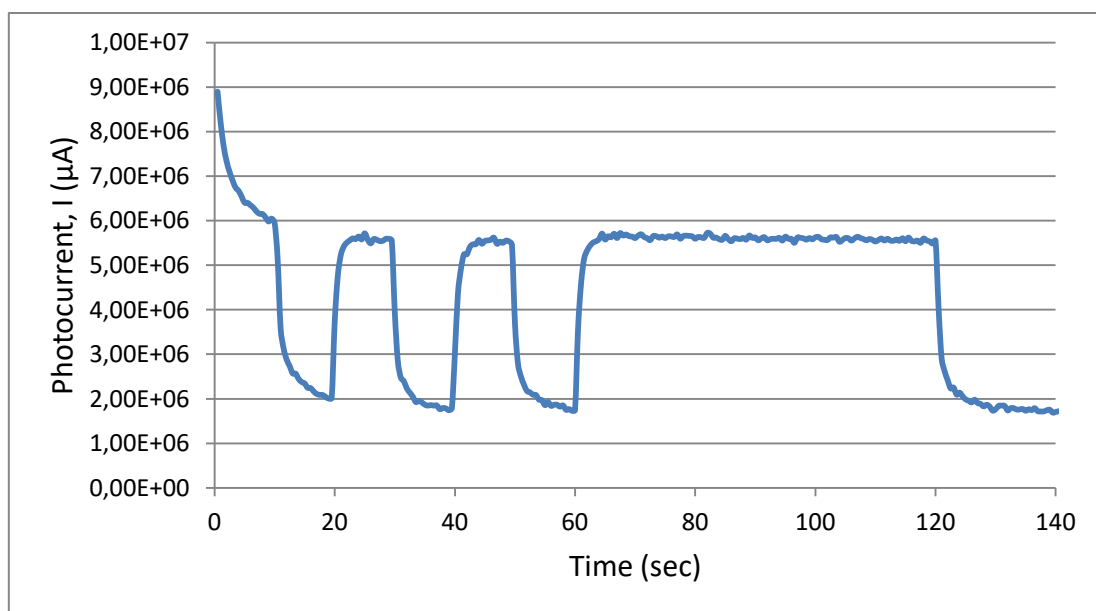


**Figure 13.** Compare  $U$  front  $I$  between exposure ultraviolet and without it (30 min of previous treatment).

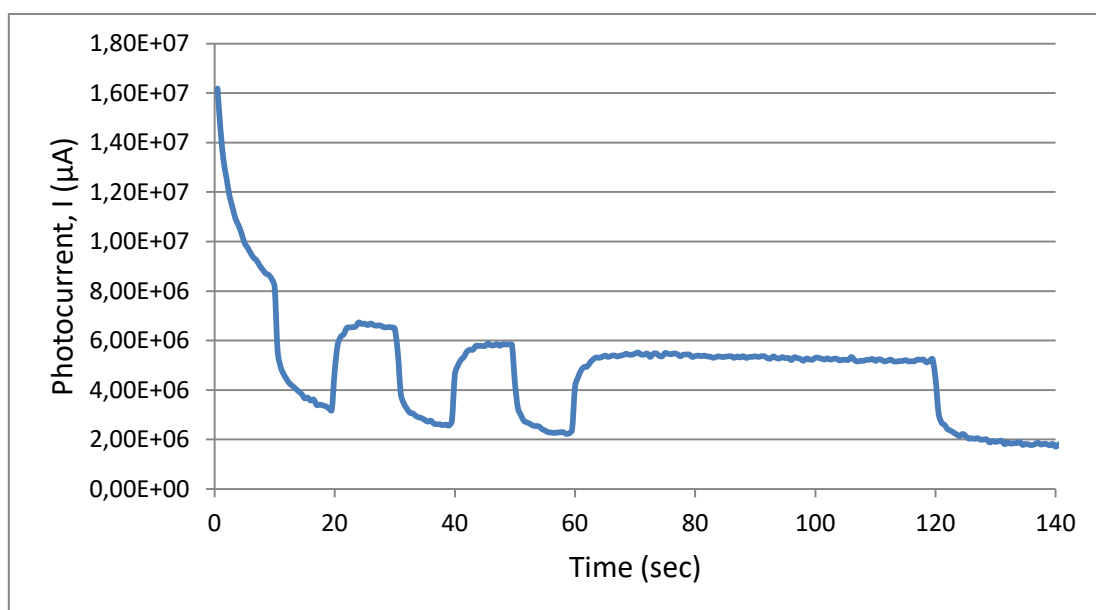
In this graphics we can see how the intensity is increasing at the same time with the voltage in an exponential way. Also, we can see the samples treated with ultraviolet light previously can give results higher with the same voltage. The greater the treatment, the greater the intensity obtained at the end. We can see too the difference between the light ultraviolet exposition and without, and the evolution of the intensity respect voltage. It is the case that it also increases depending on whether it has been previously treated or not, giving finally higher results with the treatment.

#### 4.1.2. Test changing exposure UV light every 10 seconds

Another test consist in a amperometry, measure the evolution of the intensity in function of the time, varied every 10 seconds the ultraviolet exposition and, finally, leave the light 60 seconds to check the regularity of the intensity, and 20 seconds without. The voltage is constant with 1V. The mostly next test is going to using this way.

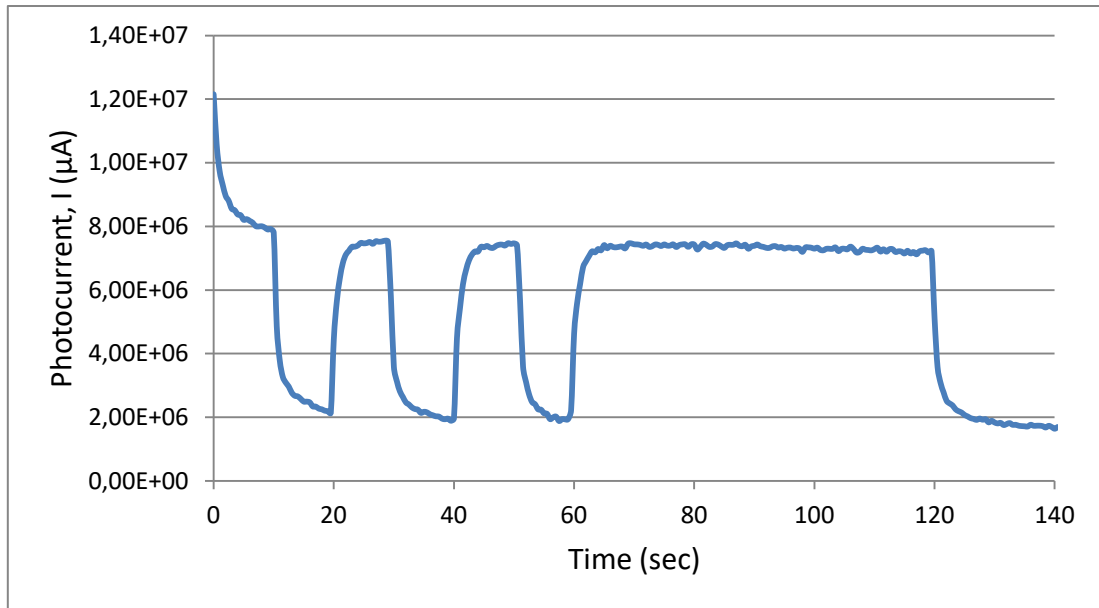


**Figure 14.** Test changing exposure ultraviolet every 10sec (0 min of previous treatment).

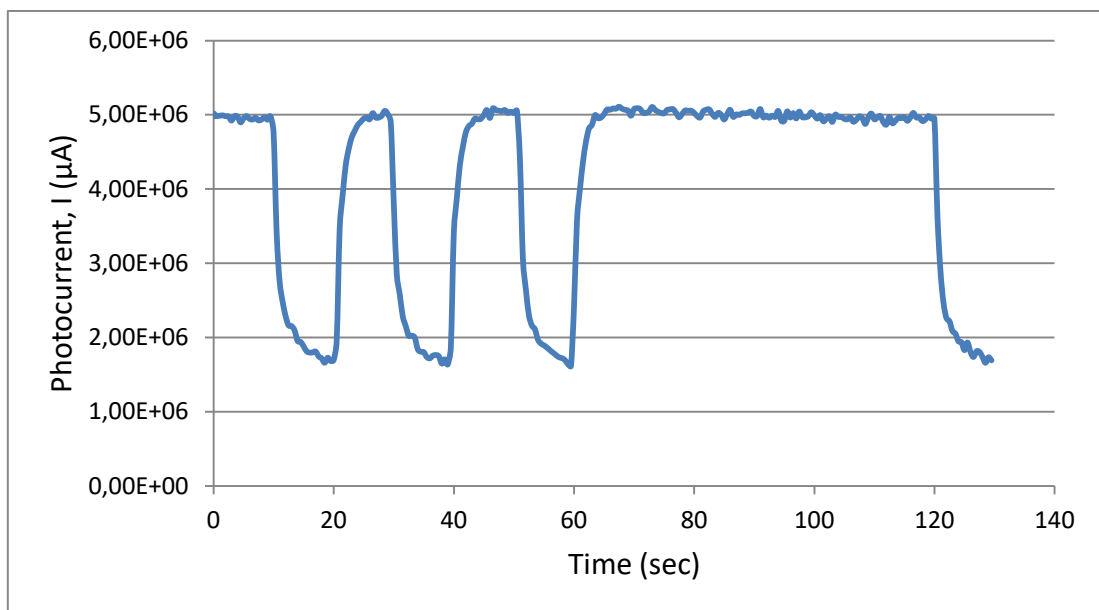


**Figure 15.** Test changing exposure ultraviolet every 10sec (10 min of previous treatment).





**Figure 16.** Test changing exposure ultraviolet every 10 seconds (20 min of previous treatment).



**Figure 17.** Test changing exposure ultraviolet every 10 seconds (30 min of previous treatment).

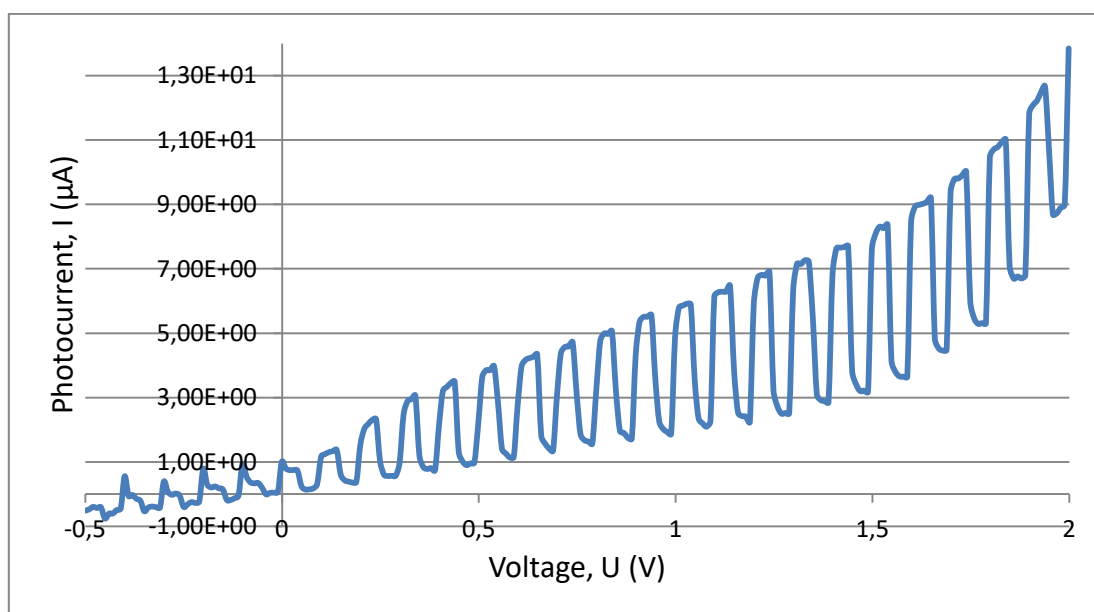
In this graphics we can see the changes produced when change the light ultraviolet exposure on the electrode, while it is applied a electricity with the same difference of voltage. We see how the intensity in respect with the time is changing increased when the light is applied and decreasing when it has not. The test start with a overcurrent until it is stabilized.

We leave when the test is in the first minute another minute of light to see how evolves the current and if it keeps stable, because in the changes the stabilization start but it is not enough. The same thing is when it has not light, we leave the last 20 seconds to see how the current is constant.

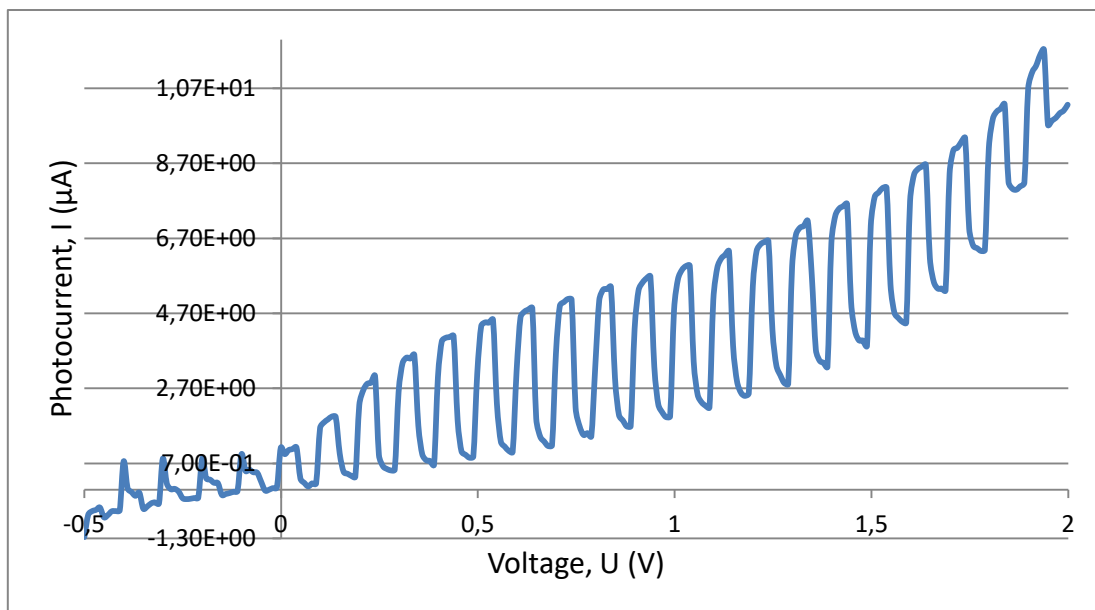
In this test we should see how the current increases in the light projection on the samples which previously was treated with ultraviolet light. We can see it doesn't happen, been lower the maxim intensity on the sample with 30 minutes in compare with the sample with 20 minutes of treatment. In the future we will work with this test, but for every previous treatment we will using a higher number of samples to calculate the average, because it sometimes doesn't work how we want.

#### 4.1.3. Test changing exposure UV light every 0.05V

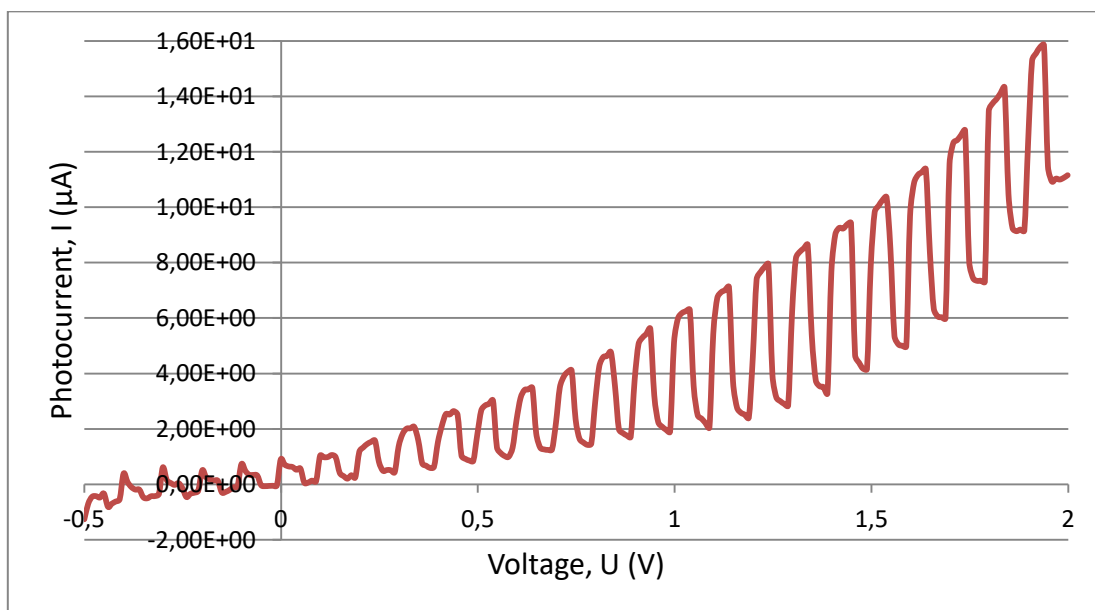
Finally, measure the intensity in function of the voltage, changing the exposition of the light every 5mV of difference, since -0.5V to 2V. The finals results of this graphics look like to the first test.



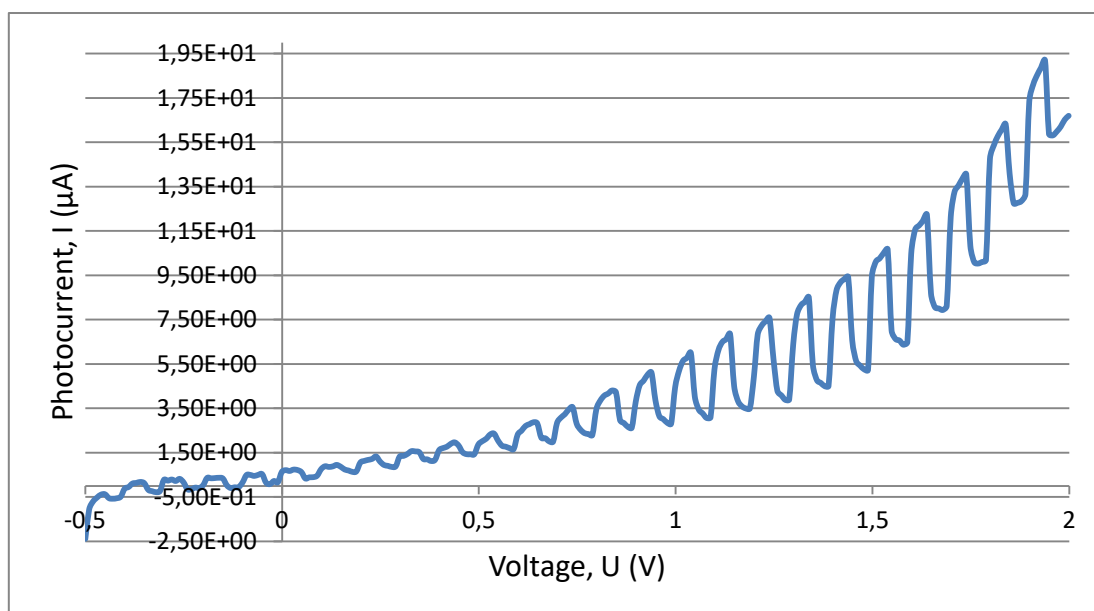
**Figure 18.** Test changing exposure ultraviolet every 0.05V (0 min of previous treatment).



**Figure 19.** Test changing exposure ultraviolet every 0.05V (10 min of previous treatment).



**Figure 20.** Test changing exposure ultraviolet every 0.05V (20 min).



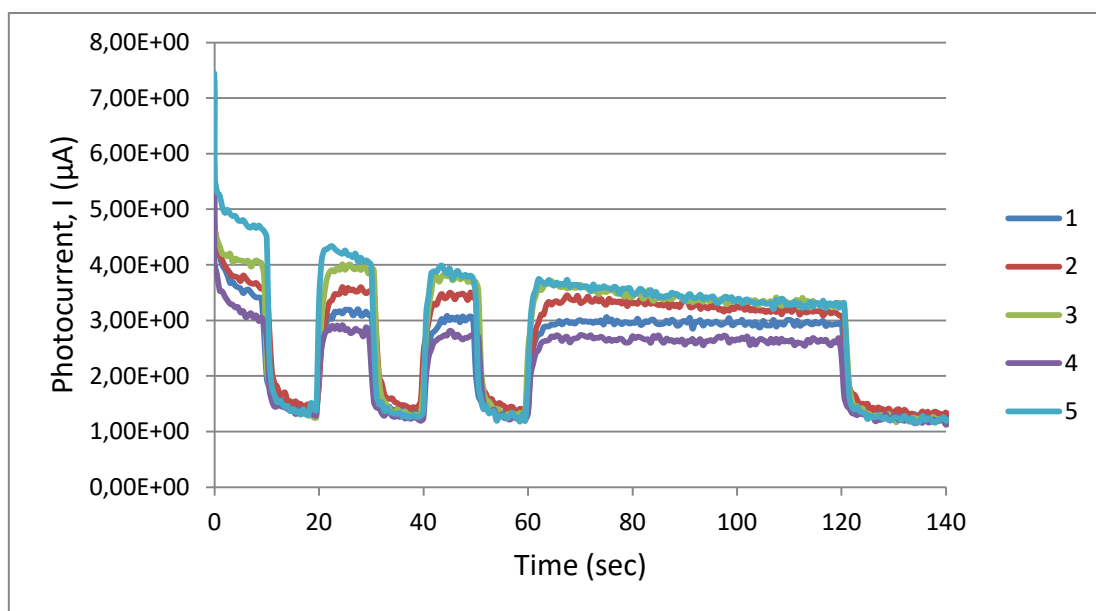
**Figure 21.** Test changing exposure ultraviolet every 0.05V (30 min of previous treatment).

Starting since -0.5V, we see how the intensity is increasing depends if the ultraviolet light is projecting or not. We can see how is making peaks every time the light is projecting and the evolution of the intensity, watching the points, is similar at the first test where we left the light to see the intensity how was increasing. The test changing exposure ultraviolet every 5V y the Compare exposure with ultraviolet and without are realized to check the functioning of the work method and check if the electrodes the Ohm law because when we increase the voltage, or potential, the intensity increase too, with the same resistance.

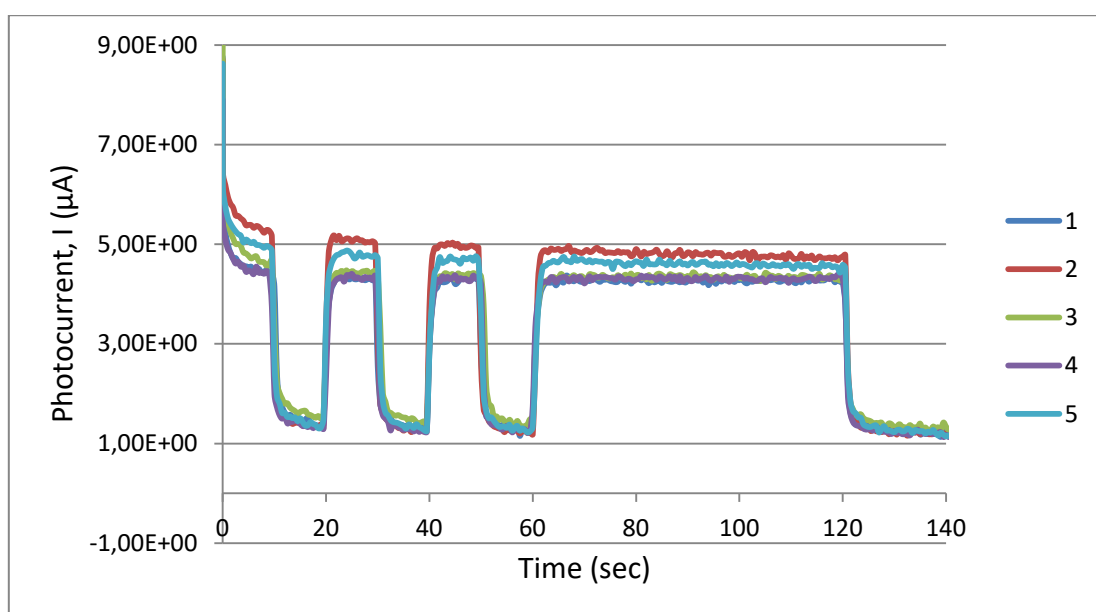
#### **4.2. Photocurrent measures with 40µm distances samples with a previous treatment over the water floating**

##### **4.2.1. Firsts tests**

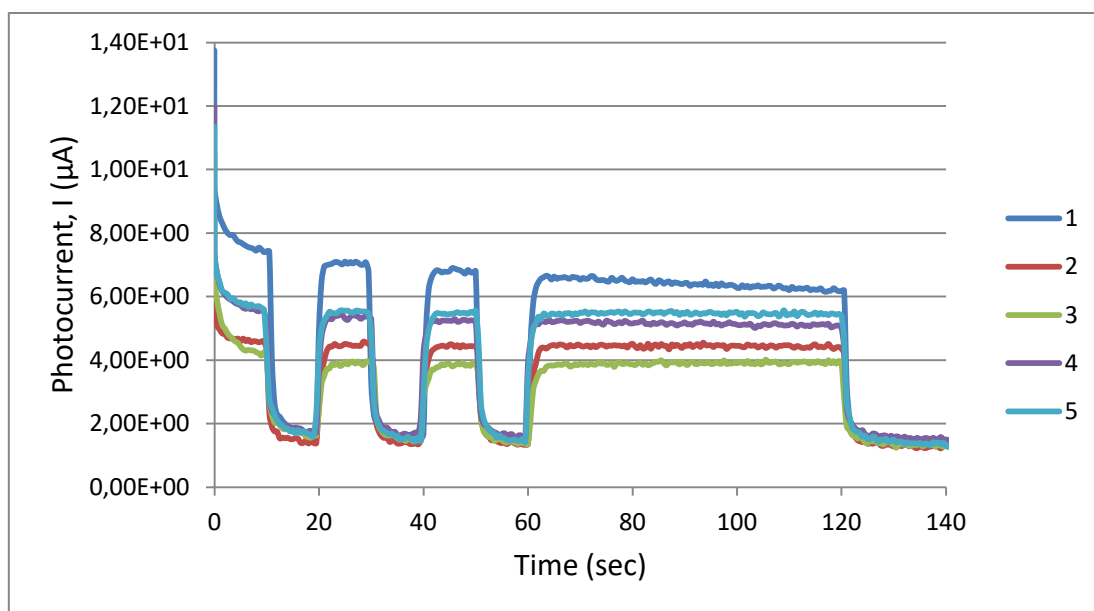
We've prepared a samples to work with the test changing every 10 seconds. They are samples with a previous treatment of the ultraviolet light 10, 20 and 30 minutes. Five samples for every time, including the samples which was not treated (0 min). We realize the amperometry with this samples, I (µA) in function of the time.



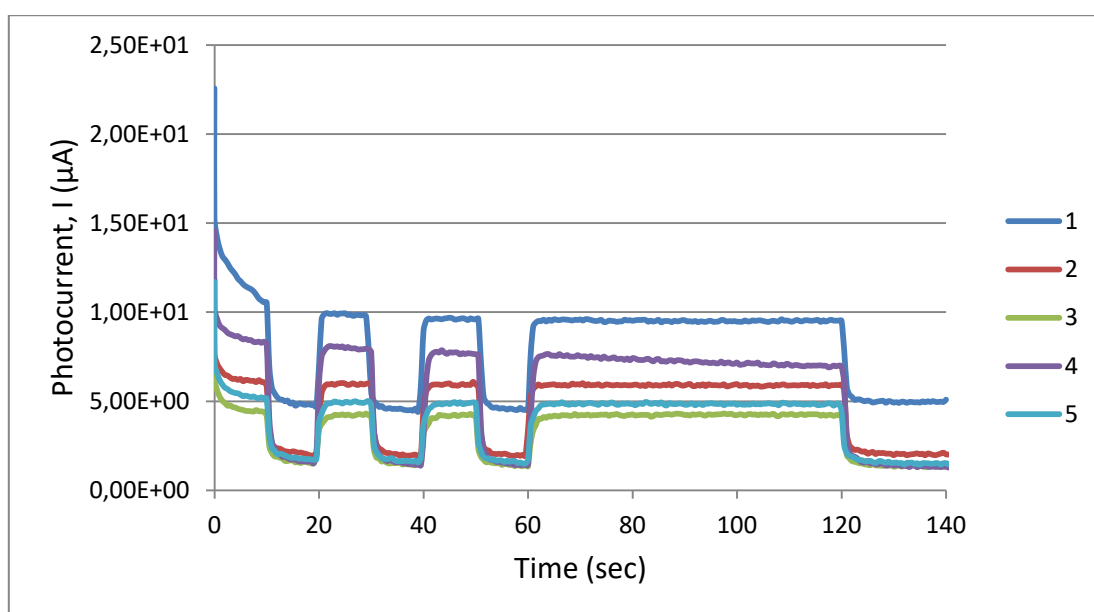
**Figure 22.** Photocurrent measures of sample with 40µm distance of the drops (0 min of previous treatment).



**Figure 23.** Photocurrent measures of sample with 40µm distance of the drops (10 min of previous treatment).



**Figure 24.** Photocurrent measures of sample with 40µm distance of the drops (20 min of previous treatment).



**Figure 25.** Photocurrent measures of sample with 40µm distance of the drops (30 min of previous treatment).

Here with this test we start to carry out and check the best conditions of the electrodes to get a efficient maximum, because we are always going to work with amperometries. This test, as it has said before, can show a vision of how evolves the intensity over time, and in function if it is exposures to the ultraviolet light. For this reasons it is the principal test.

We start watching the sample without the previous treatment (**Figure 22**) before the amperometry. In this electrode the values of the intensity when the light is inciting are the lowest compared with the other samples, with a maximums of  $3,3\mu\text{A}$  and a minimums of  $2,6\mu\text{A}$ .

The values of the samples treated 10 minutes (**Figure 23**) present a values more stable that the previous and more adjust, between  $4,2$  and  $4,5\mu\text{A}$ . Higher that the samples without previous treatment, but lower that the samples treated 20 minutes (**Figure 24**).

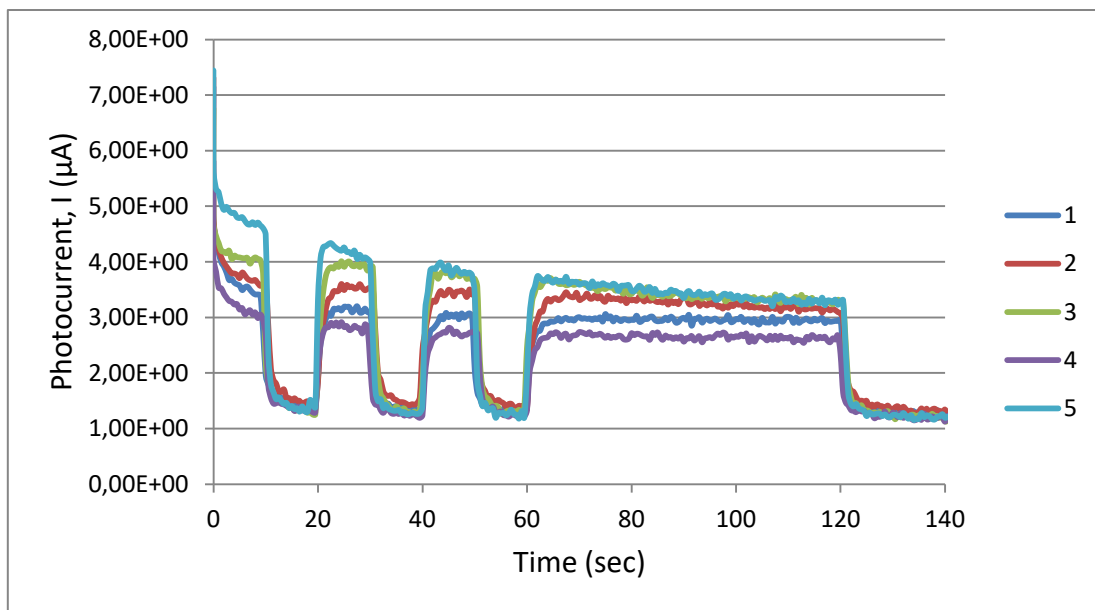
The samples treated 20 minutes (**Figure 24**) don't present values more adjust than the 10 minutes, but they present higher values of current, arriving  $6.2\mu\text{A}$ , with a minimum of  $4\mu\text{A}$ .

The samples with a previous treatment of 30 min (**Figure 25**), the samples with the highest treatment, present the higher values of intensity arriving  $9.5\mu\text{A}$ .

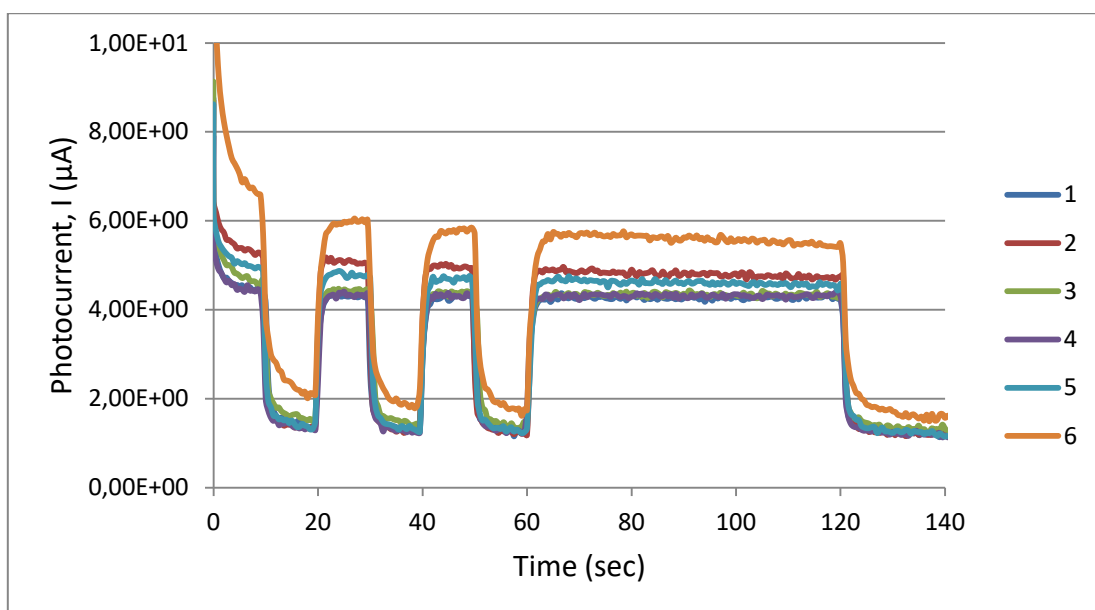
This means that the greater treatment with ultraviolet light, before the test, the higher intensity reached.

#### **4.2.2. Added a 6th sample and calculate of standard deviation**

We include one more sample (6 in total) in the test for every time, for realize a average and a standard deviation of the values between the finals seconds when it is applied the ultraviolet light during the 60 seconds (100 and 120 seconds). Then, It represents the standard deviation of the four intervals in function of the time.

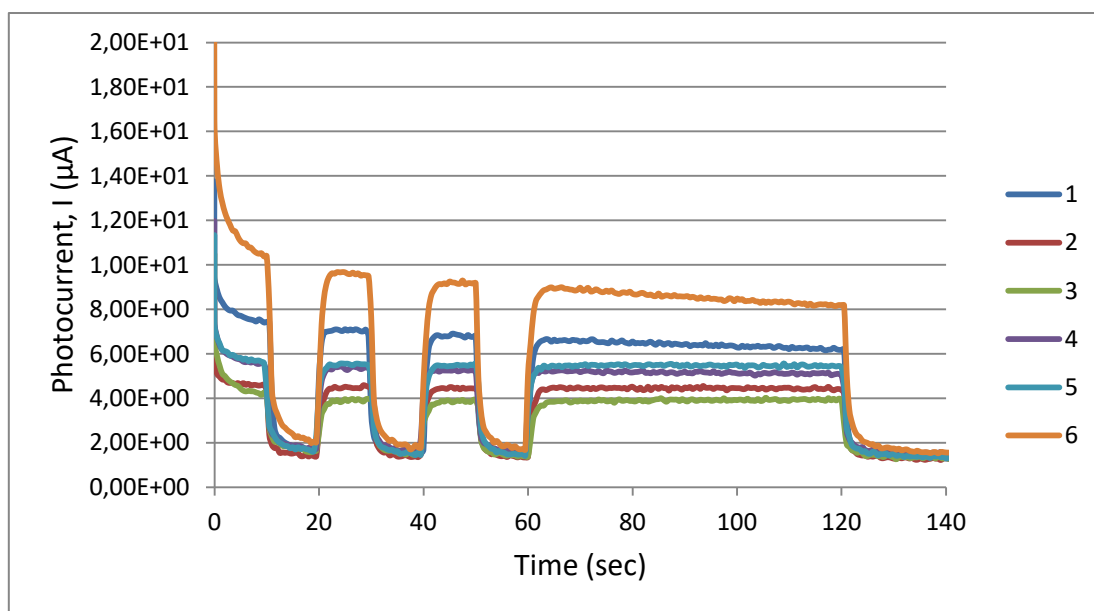


**Figure 26.** Photocurrent measures of sample with  $40\mu\text{m}$  distance of the drops (0 min of previous treatment).

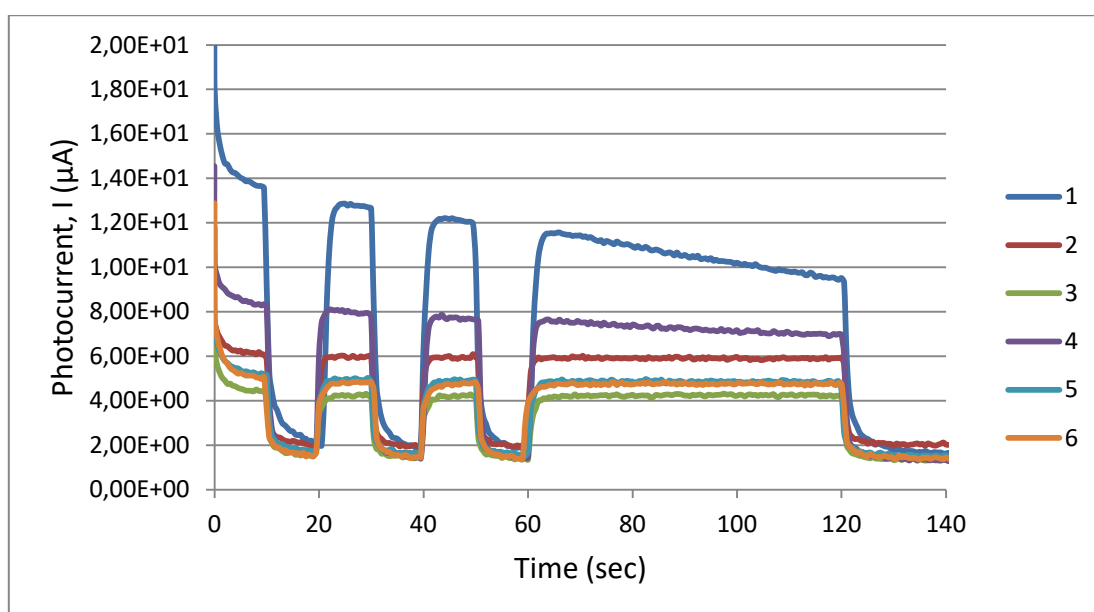


**Figure 27.** Photocurrent measures of sample with  $40\mu\text{m}$  distance of the drops (10 min of previous treatment).





**Figure 28.** Photocurrent measures of sample with 40µm distance of the drops (20 min of previous treatment).



**Figure 29.** Photocurrent measures of sample with 40µm distance of the drops (30 min of previous treatment).

In the **Figure 26** we can see the sample added is too much high. So we ignore this sample for calculate the standard deviation. The sample added in the **Figure 27** is very similar than the other, so it is not a problem. In the **Figure 28** we watch the sample added is very similar too.

The sample added in the **Figure 29** is equal to the others, adjusting to the corresponding values, but we have a problem with one sample (1) which is very deviated.

**Table 1.** Averages and standard deviation of sample with 40 $\mu$ m distance of the drops (0 min of previous treatment).

Average 1	2,95E+00
Average 2	3,17E+00
Average 3	3,31E+00
Average 4	2,62E+00
Average 5	3,31E+00
Total average ( $\mu$ A)	3,07E+00
Standard deviation	0,29

**Table 2.** Averages and standard deviation of sample with 40 $\mu$ m distance of the drops (10 min of previous treatment).

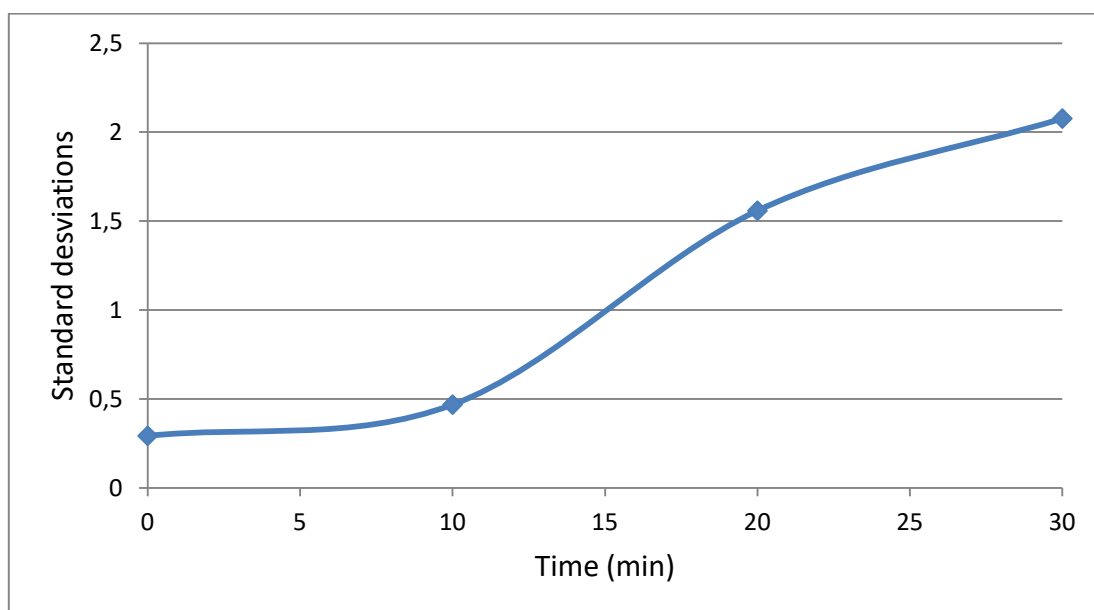
Average 1	4,28E+00
Average 2	4,75E+00
Average 3	4,34E+00
Average 4	4,31E+00
Average 5	4,56E+00
Average 6	5,51E+00
Total average ( $\mu$ A)	4,62E+00
Standard deviation	0,46

**Table 3.** Averages and standard deviation of sample with 40 $\mu$ m distance of the drops (20 min of previous treatment).

Average 1	6,26E+00
Average 2	4,43E+00
Average 3	3,92E+00
Average 4	5,10E+00
Average 5	5,45E+00
Average 6	8,29E+00
Total average ( $\mu$ A)	5,58E+00
Standard deviation	1,55

**Table 4.** Averages and standard deviation of sample with 40 $\mu$ m distance of the drops (30 min of previous treatment).

Average 1	9,81E+00
Average 2	5,89E+00
Average3	4,24E+00
Average 4	7,04E+00
Average 5	4,84E+00
Average 6	4,76E+00
Total average ( $\mu$ A)	6,10E+00
Standard deviation	2,07



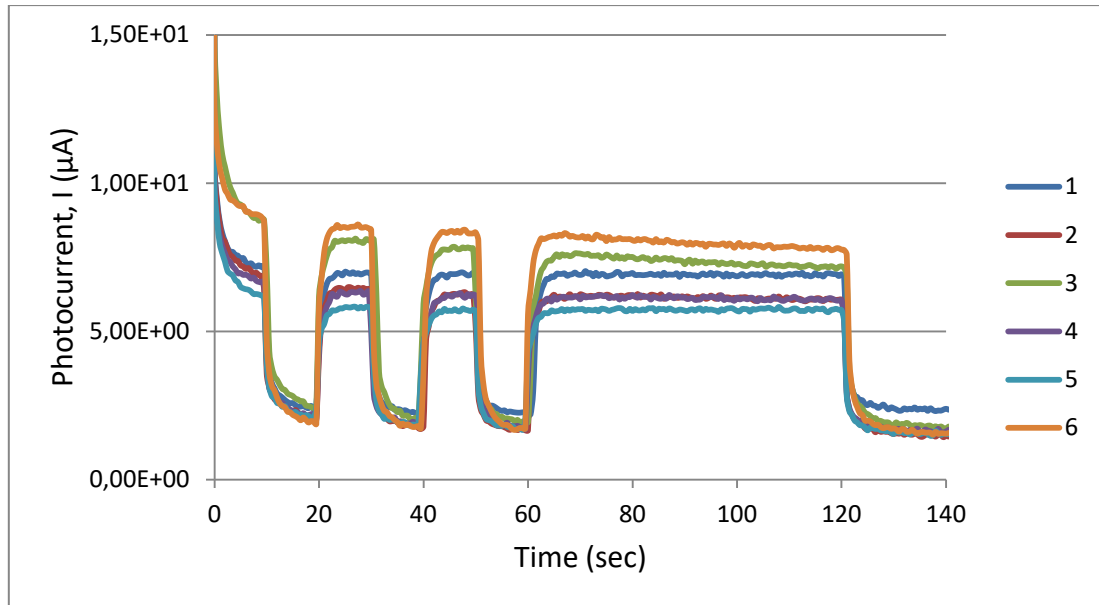
**Figure 30.** Standard deviations in front of time (min) of the 40 $\mu$ m distances samples.

We observe in the **Figure 30** the standard deviations are increasing as higher previous treatment is.

#### 4.2.3. Test of a samples previous treated 50 minutes

I have adjust the graphics with the correct axis and I have corrected the average and the standard deviation. We observe the time graphic with the averages of stabilization of the samples to every minute and, for conform the stabilization from the previous treatment of 30 minutes (**Figure 29**), we take samples without treatment and we applied ultraviolet light as previous treatment 50 minutes. We realize a normal amperometry with this samples and we include the averages and the standard deviation in the graphics to compare and observe the evolution of the averages.

We can see the screen printing on the sample is almost stabilized. In conclusion, with a previous treatment of a period of time between 30 until 50 minutes, we get the conductance maximum in the electrodes.

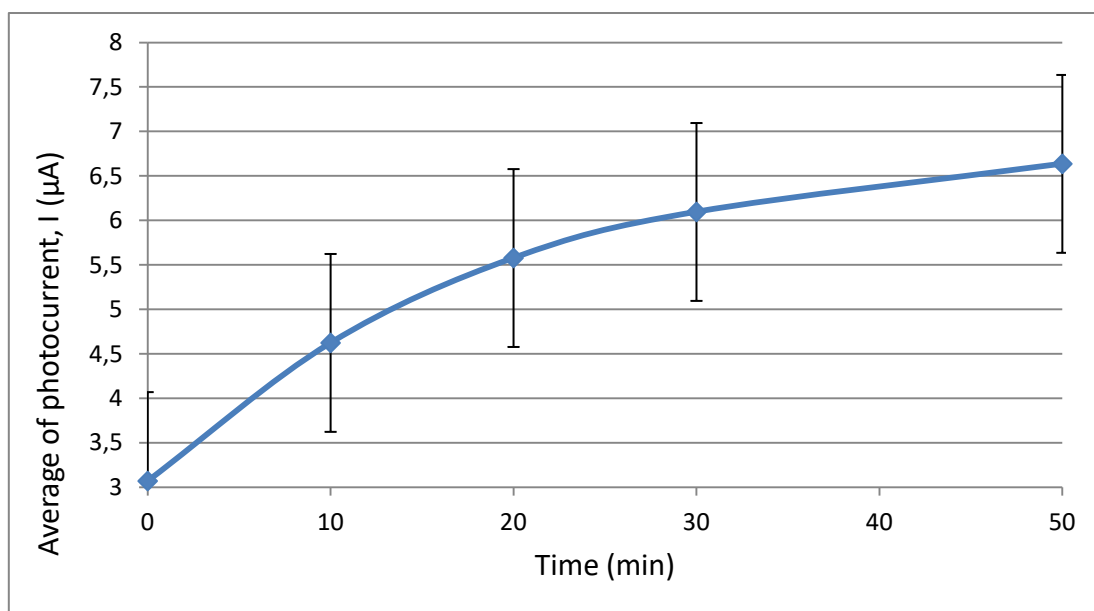


**Figure 31.** Photocurrent measures of sample with 40µm distance of the drops (50 min of previous treatment).

**Table 5.** Averages and standard deviation of sample with 40µm distance of the drops (50 min of previous treatment).

Average 1	6,91E+00
Average 2	6,08E+00
Average 3	7,21E+00
Average 4	6,07E+00
Average 5	5,73E+00
Average 6	7,83E+00
Total average (µA)	6,64E+00
Standard deviation	0,81

We can see the tendency of the averages of our samples in different times for see what time of previous treatment is better and we represent it:



**Figure 32.** Averages of the photocurrent measures ( $\mu\text{A}$ ) in front of the time (min) .

**Table 6.** Averages of samples of  $40\mu\text{m}$  comparing the time were previously treated over the water floating.

Time (min)	Average I ( $\mu\text{A}$ )
0	3,07
10	4,62
20	5,57
30	6,09
50	6,63

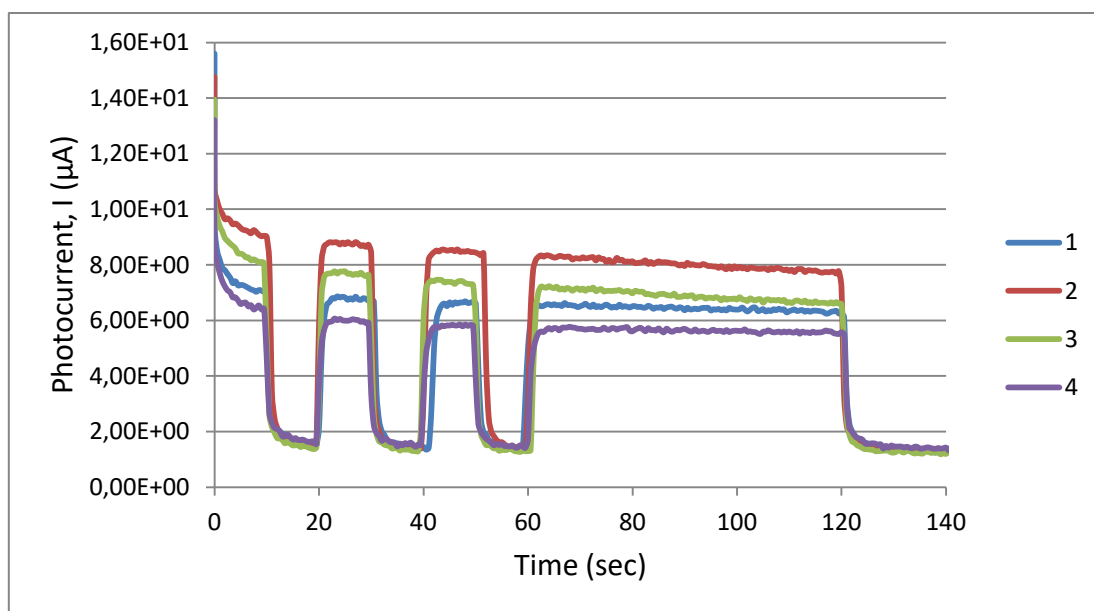
As we see on the **Figure 32** the tendency when the samples are in the minute 30 of treatment begin to stabilized a values between  $6\mu\text{A}$ , in the minute 50  $6.63\mu\text{A}$ . For this, give it a higher treatment with a bigger time it wouldn't work a lot.

#### **4.3. Photocurrent measures with $40\mu\text{m}$ distances samples with a previous treatment under the water**

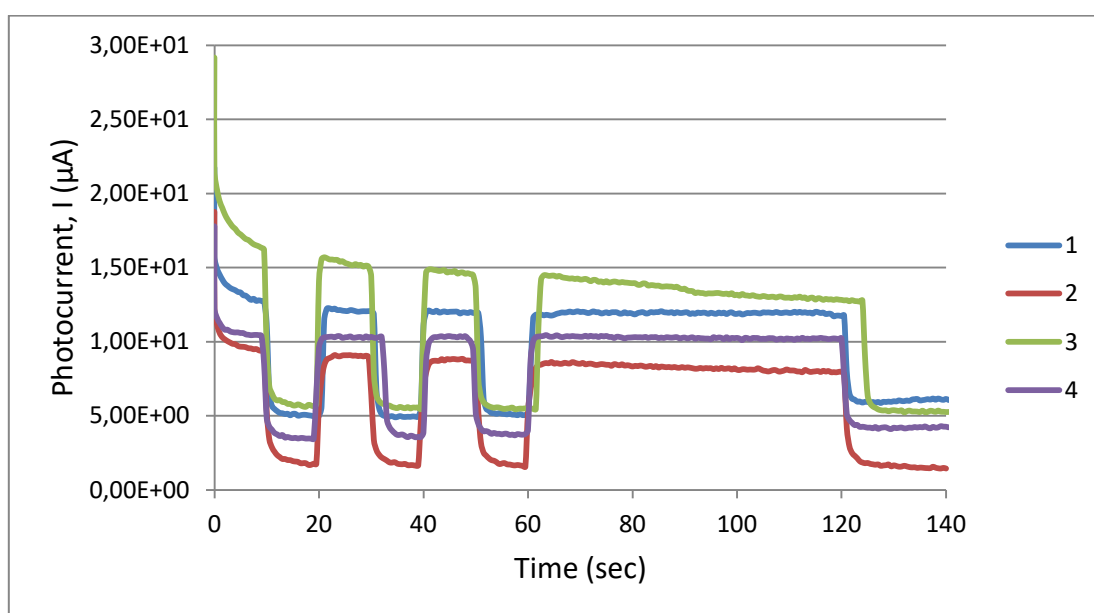
This samples were previously treated putting under the ultraviolet light in a crystallizer with a 4mm of water, but floating, not under the water covering the samples.

Then, it is prepared four samples for every time (10, 20, 30 and 50 minutes). They are treated with the same way but under the water in the crystallizer.

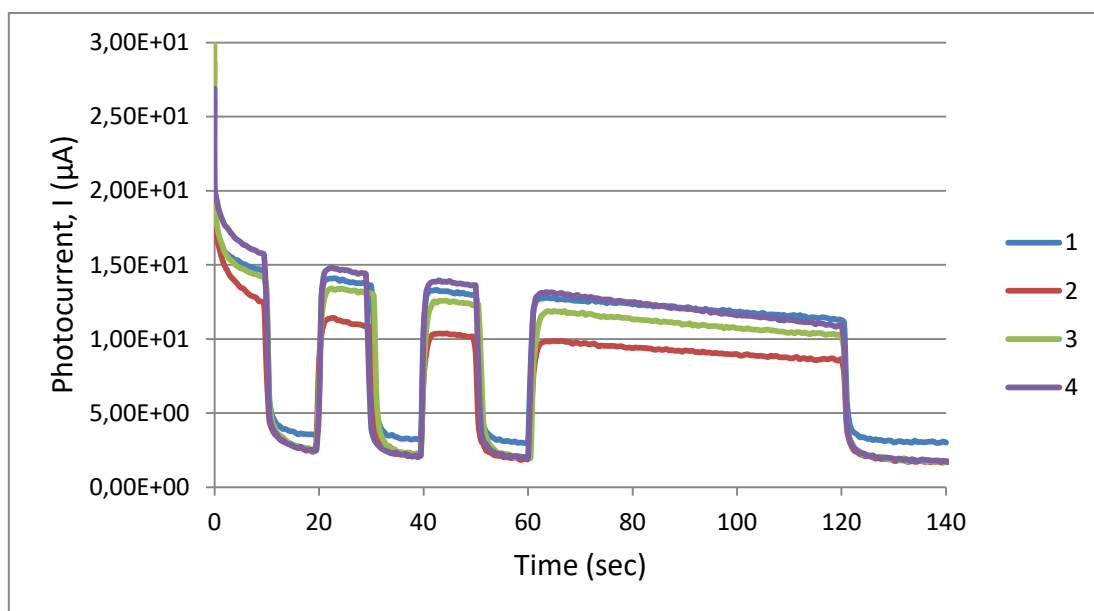
It is got, observing the results of the amperometries, a treatment under the water get a higher results.



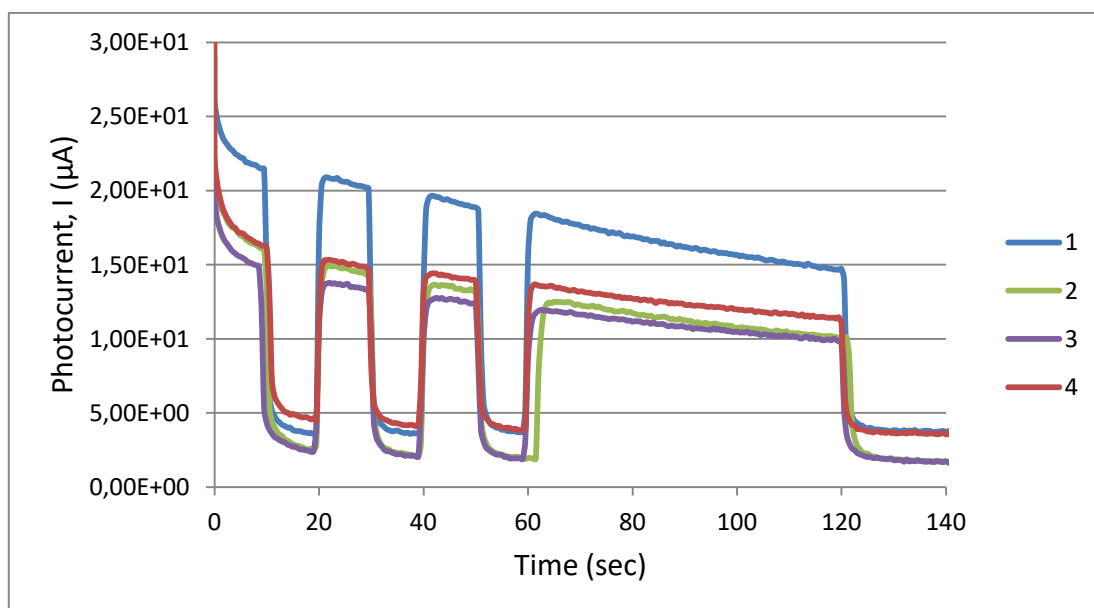
**Figure 33.** Photocurrent measures with  $40\mu\text{m}$  distance of the drops under the water (10 min of previous treatment).



**Figure 34.** Photocurrent measures with  $40\mu\text{m}$  distance of the drops under the water (20 min of previous treatment).



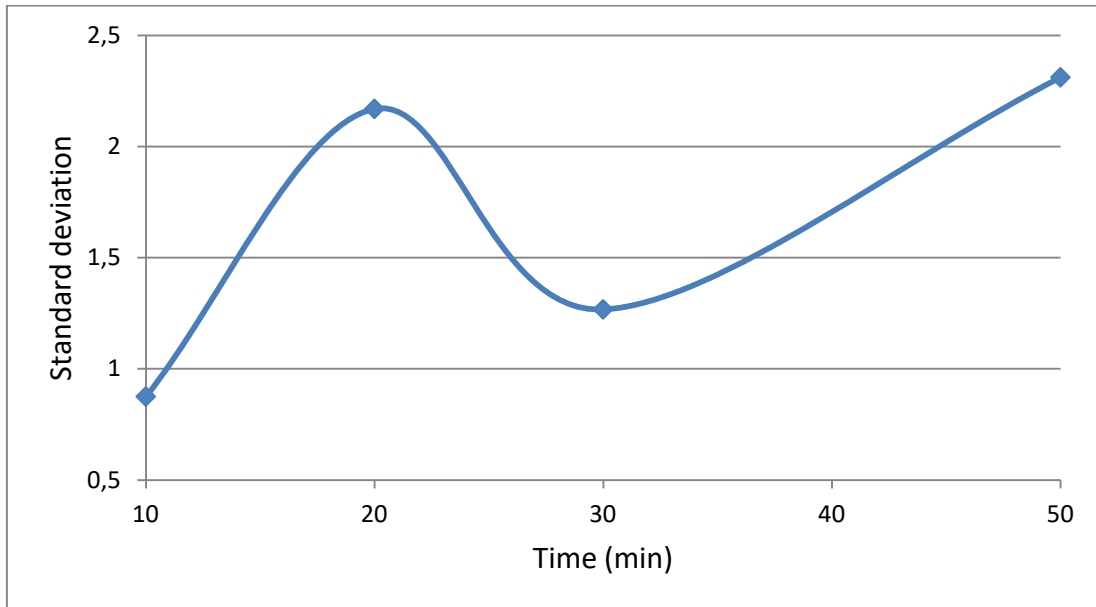
**Figure 35.** Photocurrent measures with 40µm distance of the drops under the water (30 min of previous treatment).



**Figure 36.** Photocurrent measures with 40µm distance of the drops under the water (50 min of previous treatment).

In the stabilization of the amperometries we can see the tendencies of the intensity is come down when the light is irradiating. It happens in the sample of **Figure 33**, but is going to perceive when the previous treatment is higher. Also, the values of

intensity when there is not light don't coincide sometimes in some samples, except in the **Figure 33**.



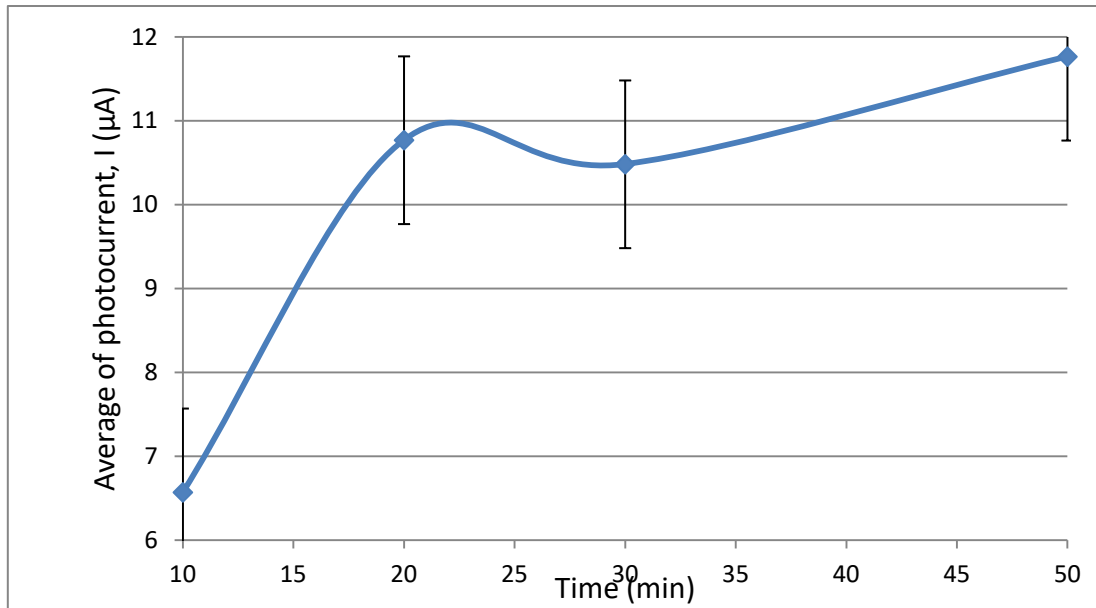
**Figure 37.** Standard deviations in front of time (min) of the 40µm distances samples.

In the next graphic we see the values of the averages of the intensity with the samples under the water:

**Table 7.** Averages of samples of 40µm comparing the time were previously treated under the water.

Time (min)	Average I (µA)
10	6,57
20	10,77
30	10,48
50	11,76

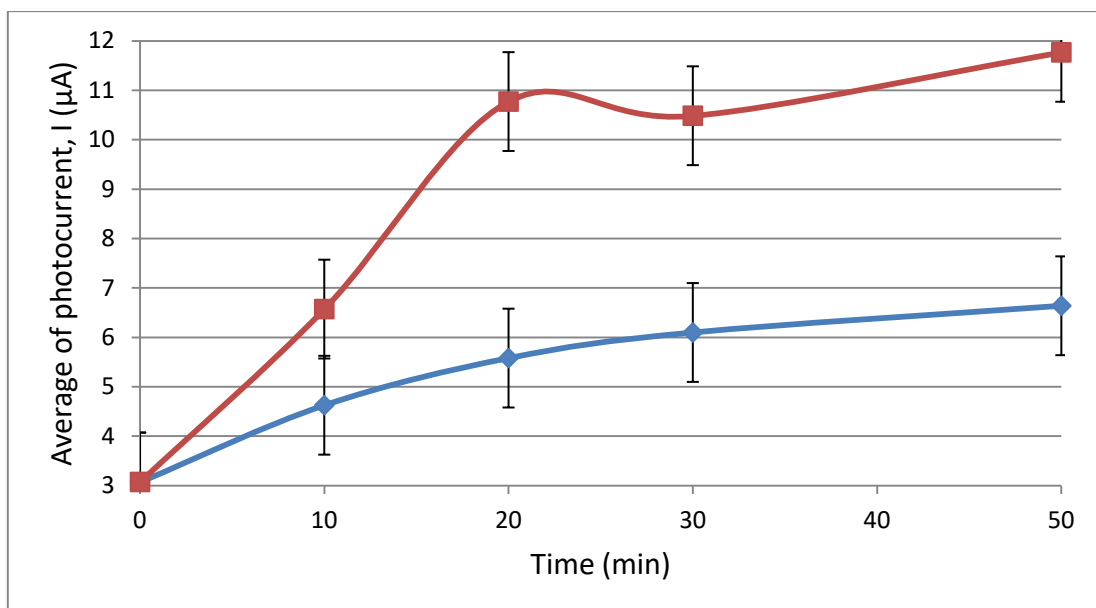




**Figure 38.** Averages of the photocurrent measures ( $\mu A$ ) in front of the time (min).

There is something that looks like a mistake in this test because the values of the samples 20 minutes are higher than the 30 minutes. This can be for a very low difference in the printing of the electrodes and the  $TiO_2$  on the samples.

Comparing the values of the graphics with both measures, with the previous treatment under the water and with the samples under, we see it is really better the treatment under the water:



**Figure 39.** Comparing averages of  $40\mu m$  samples under the water or not.

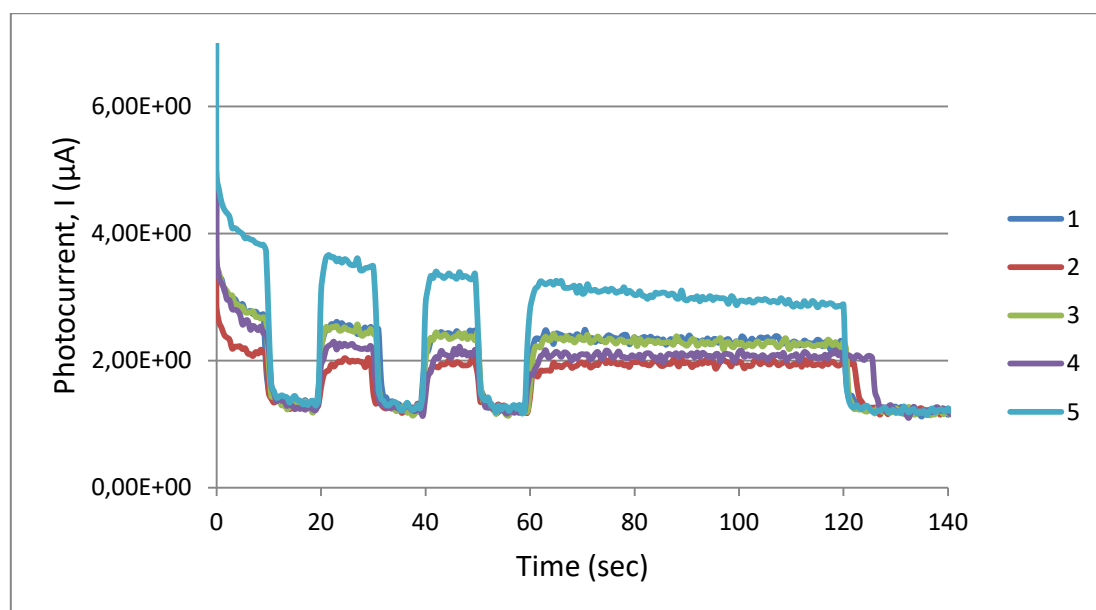
#### 4.4. Photocurrent measures with 55 and 80 $\mu\text{m}$ distances samples with a wet previous treatment

##### 4.4.1. 55 $\mu\text{m}$ distances samples

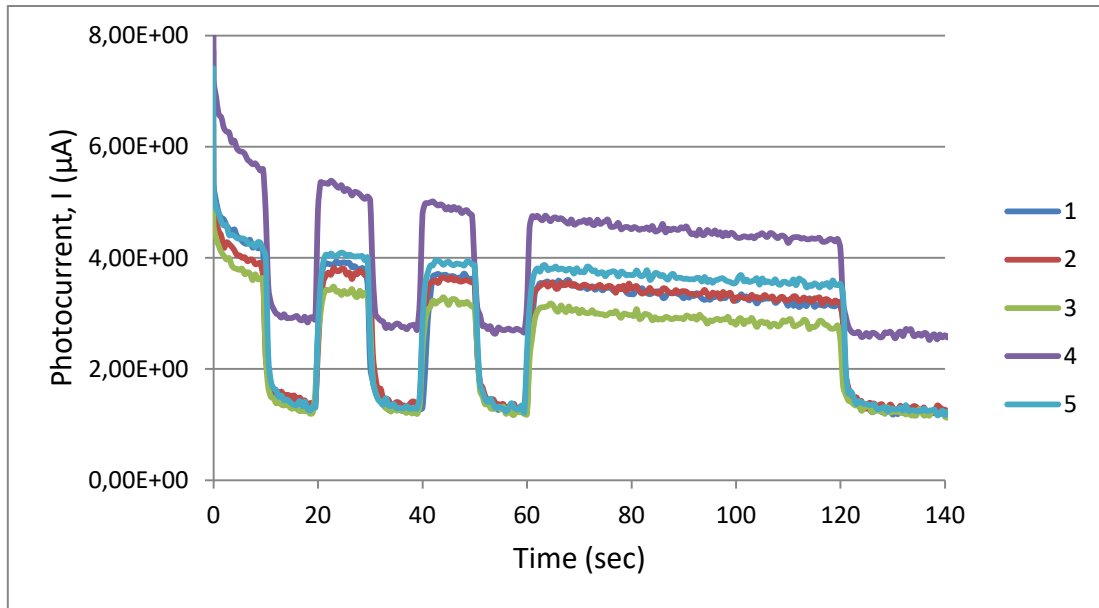
We continue the work impressing on the electrodes with different distances of the  $\text{TiO}_2$  drops, 55 and 80 $\mu\text{m}$ . Plus, 24 samples with the 40 $\mu\text{m}$  distances.

We treatment with ultraviolet light and we make an amperometry with the 55 and 80 samples, with the same way than the 40. The results are very lower than the 40, under and on the water.

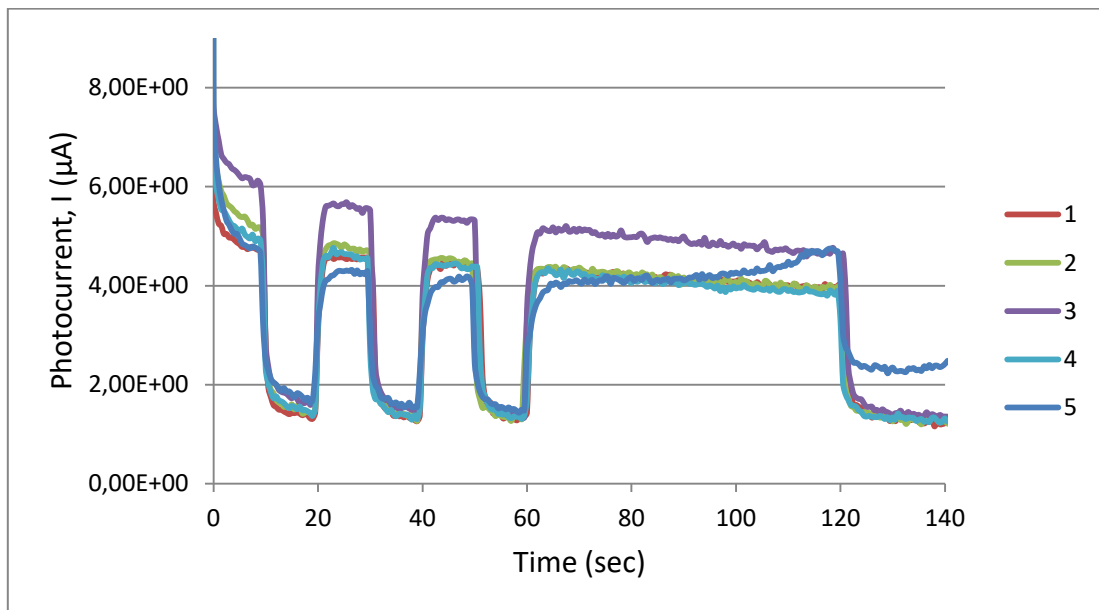
The graphics of 55 $\mu\text{m}$  distance of the  $\text{TiO}_2$  looks a little irregular because their distance between drops does interferences appear more, and the drops are more separated, so, the amount on the same surface is smaller. But still the difference of intensities on the amperometries, when the light is inciting and when not, are notables, although lower than the 40 $\mu\text{m}$  distances samples.



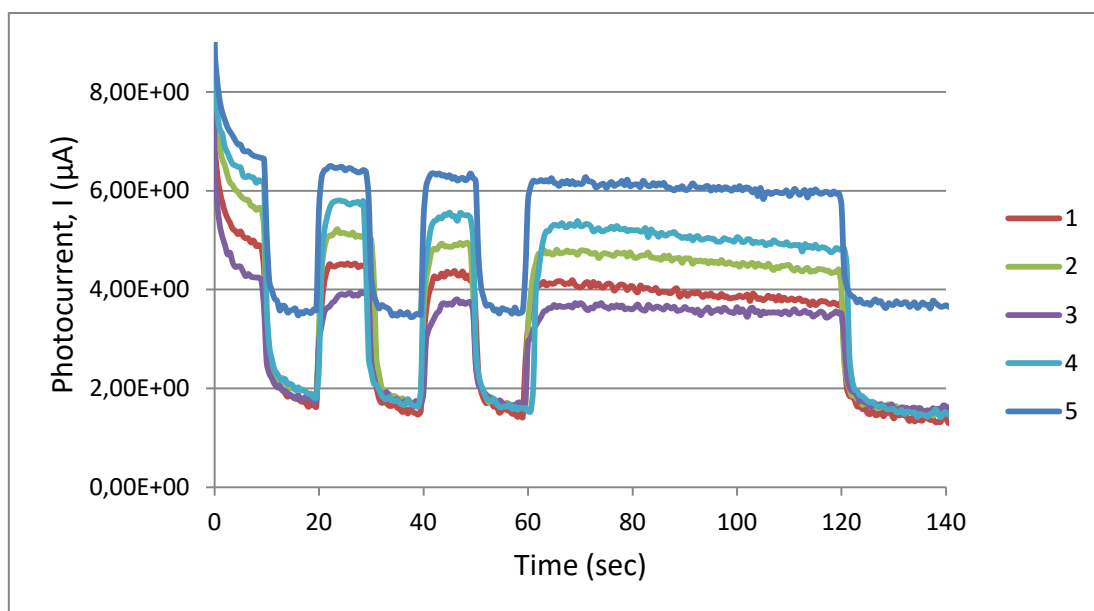
**Figure 40.** Photocurrent measures with 55 $\mu\text{m}$  distance of the drops under the water (0 min of previous treatment).



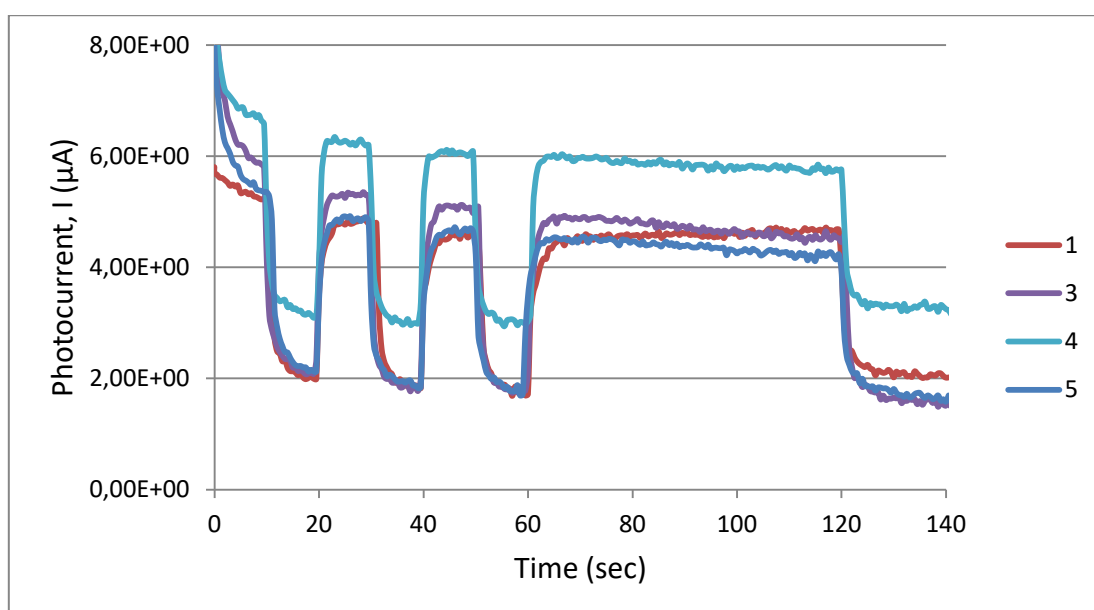
**Figure 41.** Photocurrent measures with 55µm distance of the drops under the water (10 min of previous treatment).



**Figure 42.** Photocurrent measures with 55µm distance of the drops under the water (20 min of previous treatment).



**Figure 43.** Photocurrent measures with 55µm distance of the drops under the water (30 min of previous treatment).



**Figure 44.** Photocurrent measures with 55µm distance of the drops under the water (50 min of previous treatment).

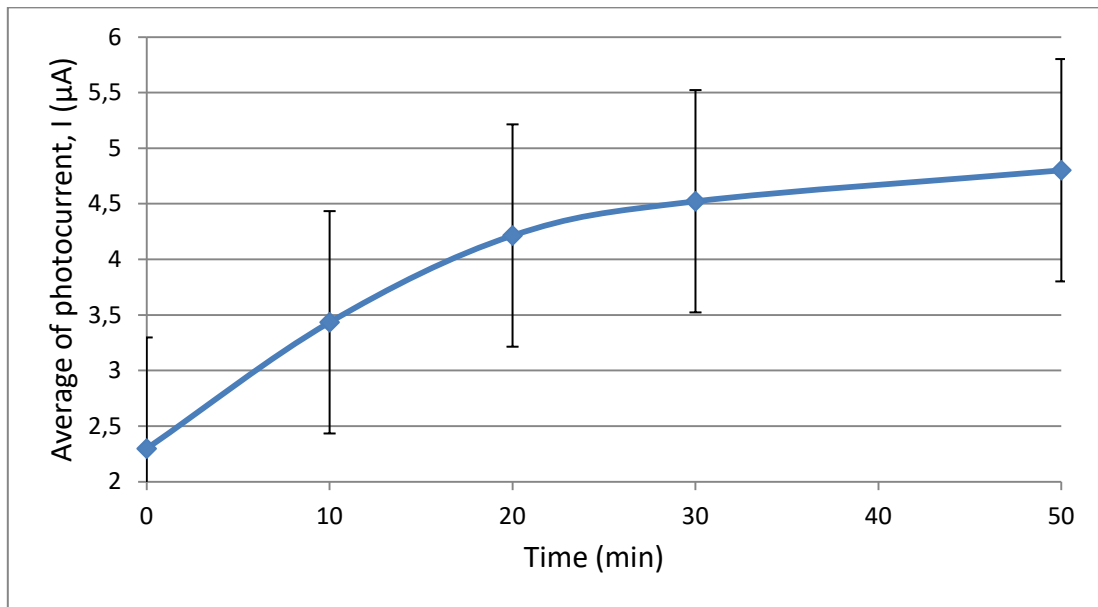
As we can see, it happens a similar situation that the 40µm distances samples, where the more time of previous treatment with ultraviolet light, higher difference of intensities it's get. The difference is the molecules of TiO<sub>2</sub> on the electrode are intertwine more quickly, for that, the amperometries are very similar at different

times, for that the maximum time of the ultraviolet light on the previous treatment is smaller.

In the next graphic we observe the averages of the samples with the 55 distance:

**Table 8.** Averages of samples of 55 $\mu$ m comparing the time were previously treated under the water.

Time (min)	Average I ( $\mu$ A)
0	2,29
10	3,43
20	4,21
30	4,52
50	4,80

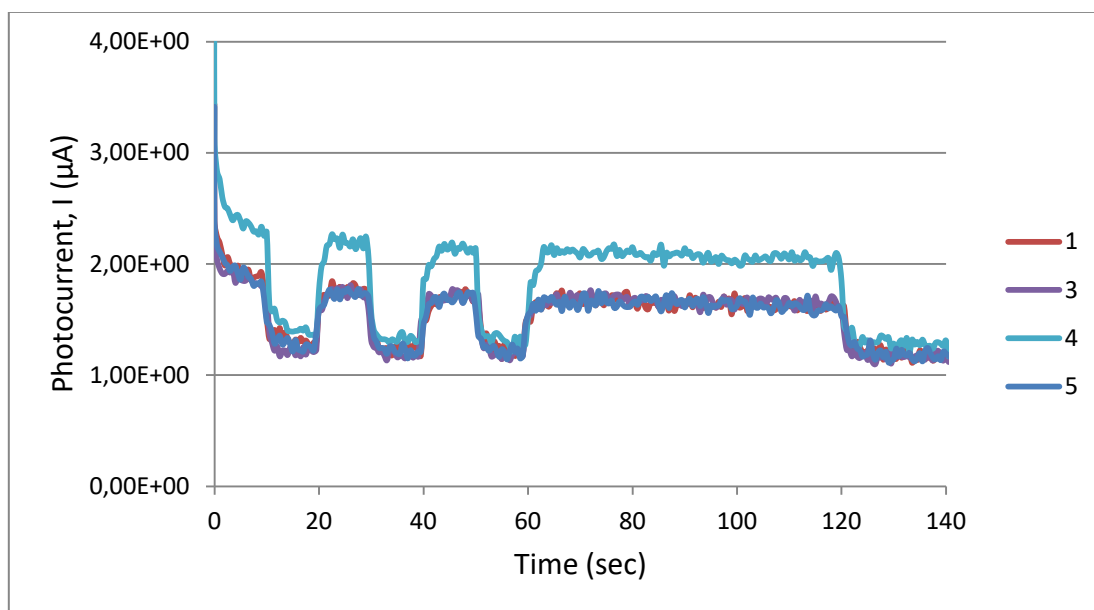


**Figure 45.** Averages of the photocurrent measures ( $\mu$ A) in front of the time (min) of 55 $\mu$ m distances samples.

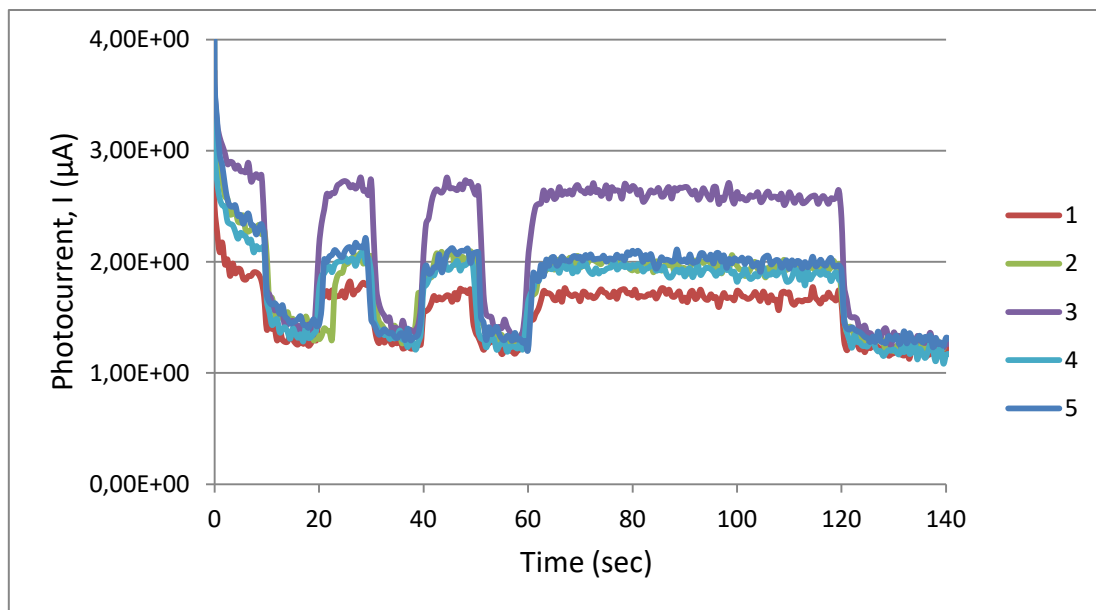
In the **Figure 45** we can see how the difference of the stabilization of the averages of the intensities of the electrodes produces before, since 20 minutes stays done practically, staying the averages between 4,21 and 4,8 $\mu$ A.

#### 4.4.2. 80 $\mu\text{m}$ distances samples

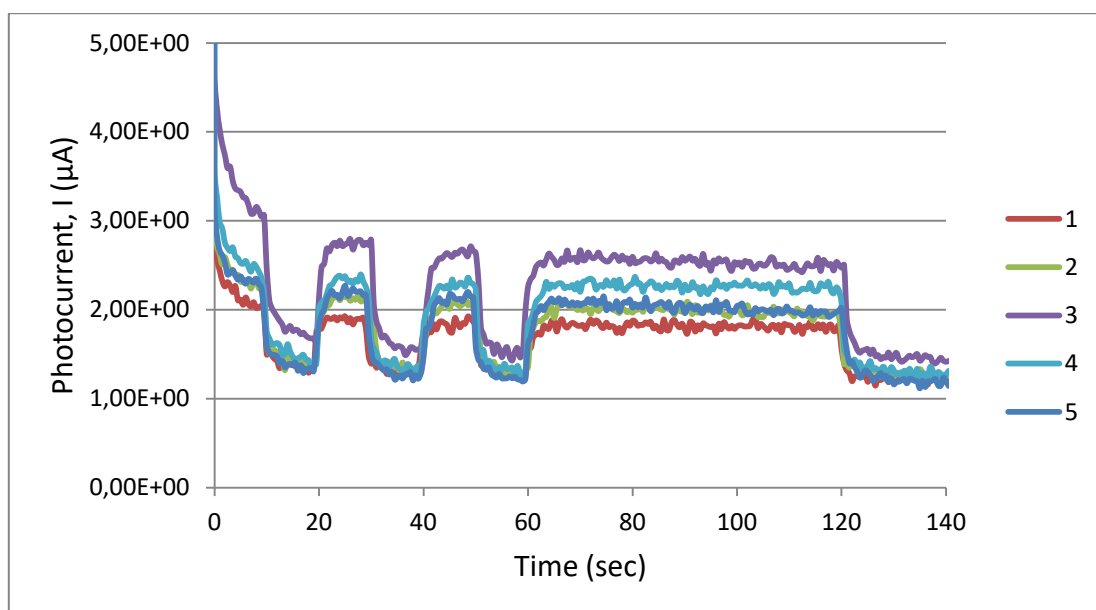
The samples with 80 $\mu\text{m}$  distances were treated with the same way. The distance between is bigger, by that, of course, the amount on the same surface is smaller still. With this samples observe the equal interferences than 55 $\mu\text{m}$  distances samples, doing the stabilization changes, but we see a clear difference between the exposition of the light and without him. Also we see how this difference is smaller. This means the intertwine of the molecules produces faster.



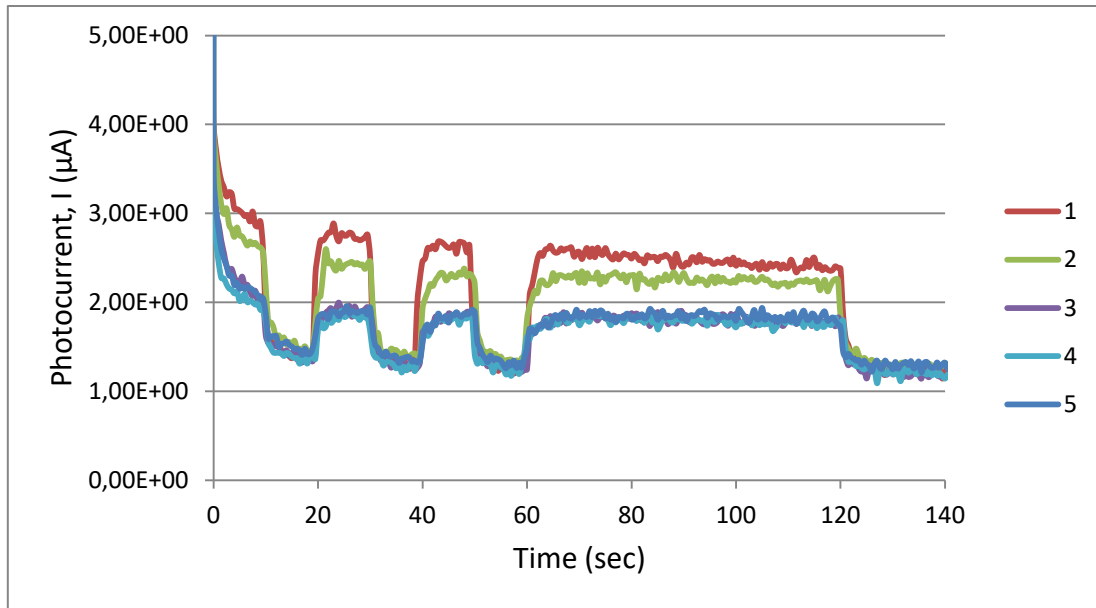
**Figure 46.** Photocurrent measures with 80 $\mu\text{m}$  distance of the drops under the water (0 min of previous treatment).



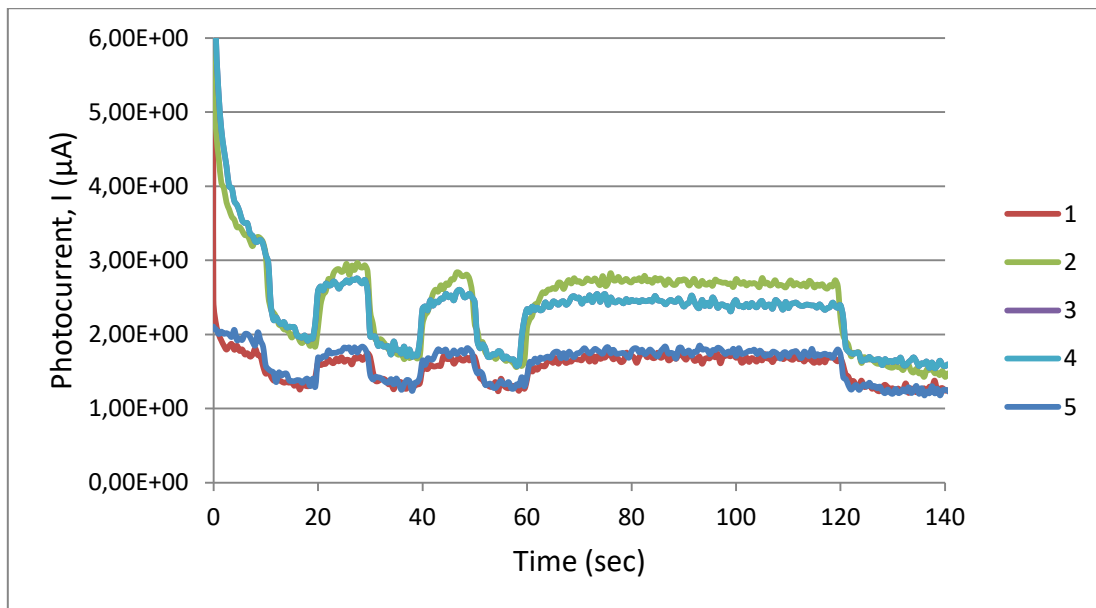
**Figure 47.** Photocurrent measures with  $80\ \mu\text{m}$  distance of the drops under the water (10 min of previous treatment).



**Figure 48.** Photocurrent measures with  $80\ \mu\text{m}$  distance of the drops under the water (20 min of previous treatment).



**Figure 49.** Photocurrent measures with 80µm distance of the drops under the water (30 min of previous treatment).



**Figure 50.** Photocurrent measures with 80µm distance of the drops under the water (50 min of previous treatment).

In this graphics we see all of them are very similar because the value of the intensity without the ultraviolet light exposition is between 1 and 2µA, while the value of the intensity with the ultraviolet light always is higher than 2µA, but it never comes to 3µA. The unique difference was the value of the intensity, in this case, in the sample without previous treatment (**Figure 46**) is very similar to 2µA, while with the treatment

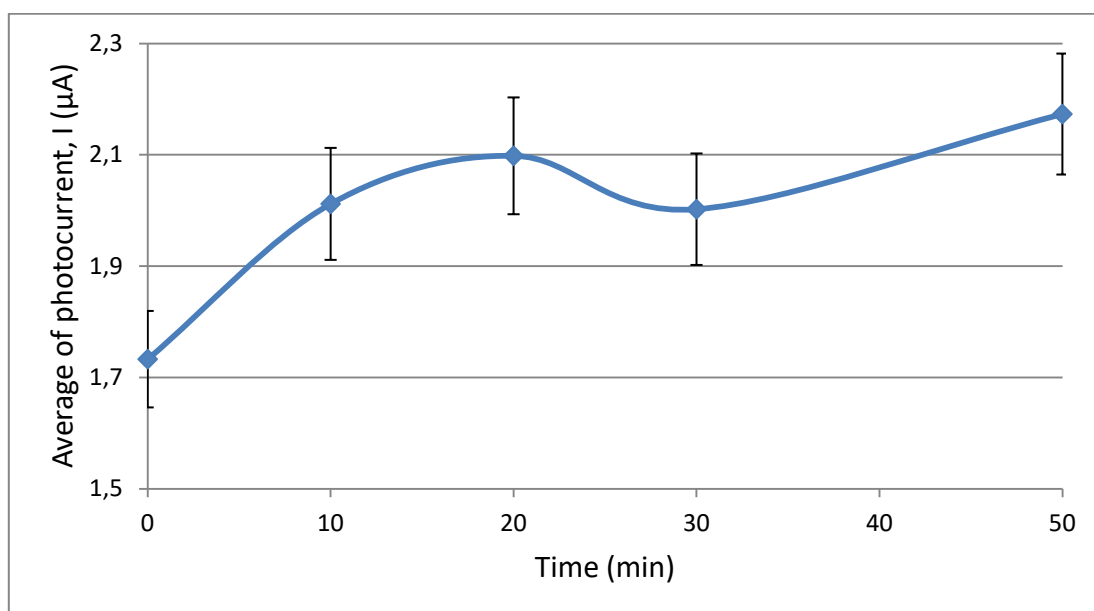


with 50 minutes (**Figure 50**) almost come to  $3\mu\text{A}$  in some samples, but this graphic is very similar to the graphics of 20 and 30 minutes (**Figure 48** and **Figure 49**).

In the next graphic we see the evolution of the averages of the intensities of 80 distance of the drops:

**Table 9.** Averages of samples of  $80\mu\text{m}$  comparing the time were previously treated under the water.

Time (min)	Average I ( $\mu\text{A}$ )
0,00E+00	1,73
1,00E+01	2,01
2,00E+01	2,09
3,00E+01	2,00
5,00E+01	2,17

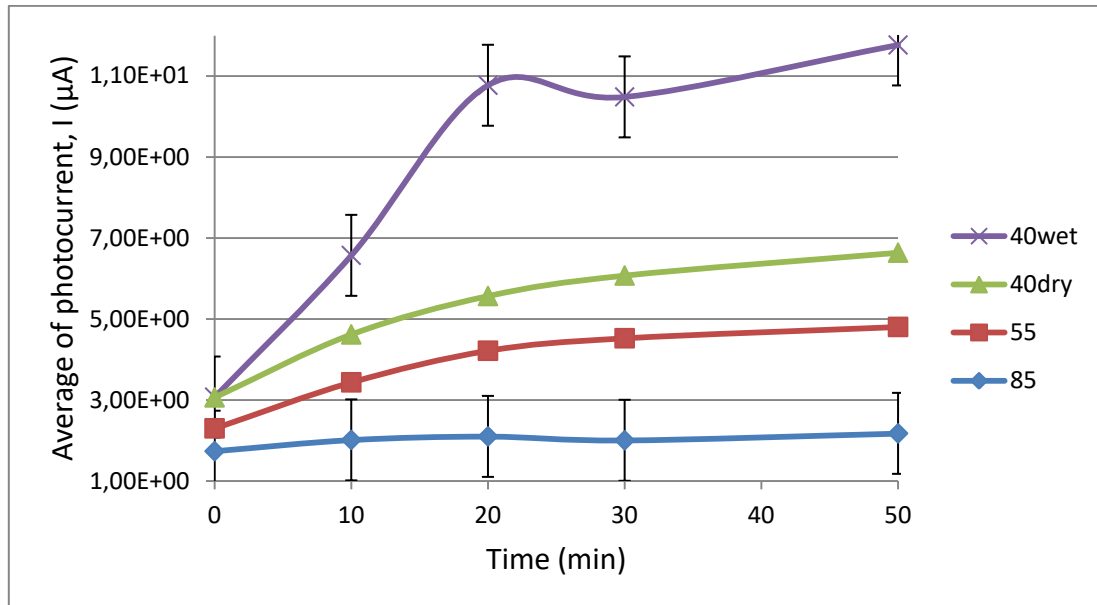


**Figure 51.** Averages of the photocurrent measures ( $\mu\text{A}$ ) in front of the time (min) of  $80\mu\text{m}$  distances samples.

We conclude in this case with a distance of  $80\mu\text{m}$ , the value of the intensity with light and without is too much low to work with him.

The difference between the samples treated 10 minutes (**Figure 47**) and 50 minutes (**Figure 50**) is around  $0,2\mu\text{A}$ , a very low value, when in the others samples with others drops distance exist higher difference. This means as for 10 minutes of previous treatment the maximum value of intensity gets with this samples.

The **Figure 52** demonstrates the averages of the all samples with the different drops distances:



**Figure 52.** Averages of the photocurrent measures ( $\mu\text{A}$ ) in front of the time (min) of all samples.

#### 4.5. Photocurrent changing the UV light distances

Calculate the photocurrent with 3 or 4 samples treated 50 minutes, but varying the distance of the lamp of ultraviolet light, checking the intensity with a radiometer, since 1.2 mW/cm; 0.9; 0.6; 0.3 and do a calibration curve of this dates.

We failure this test because the curve of calibration were very wrong.

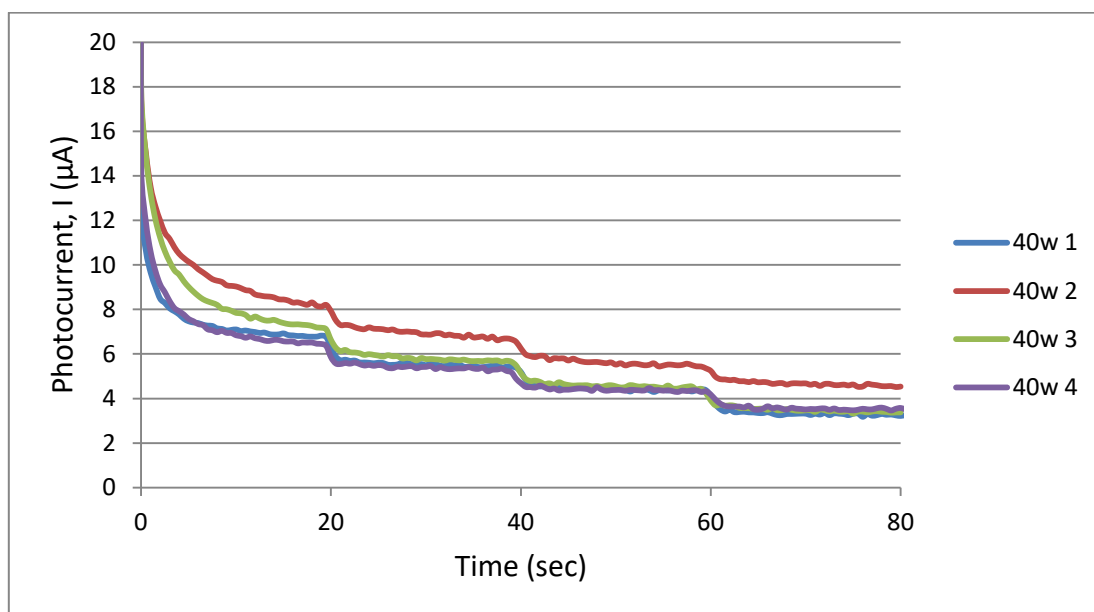
We repeat the experiment to calculate the calibrations curves but changing the distance of the lamp while the software is measuring and not every 10 seconds changing the exposition of the light. Every 20 seconds move away the lamp (when we see the current is stabilized) and see the step down of the current.

We make the average of the values at the same current and with this do the graphics of calibration.

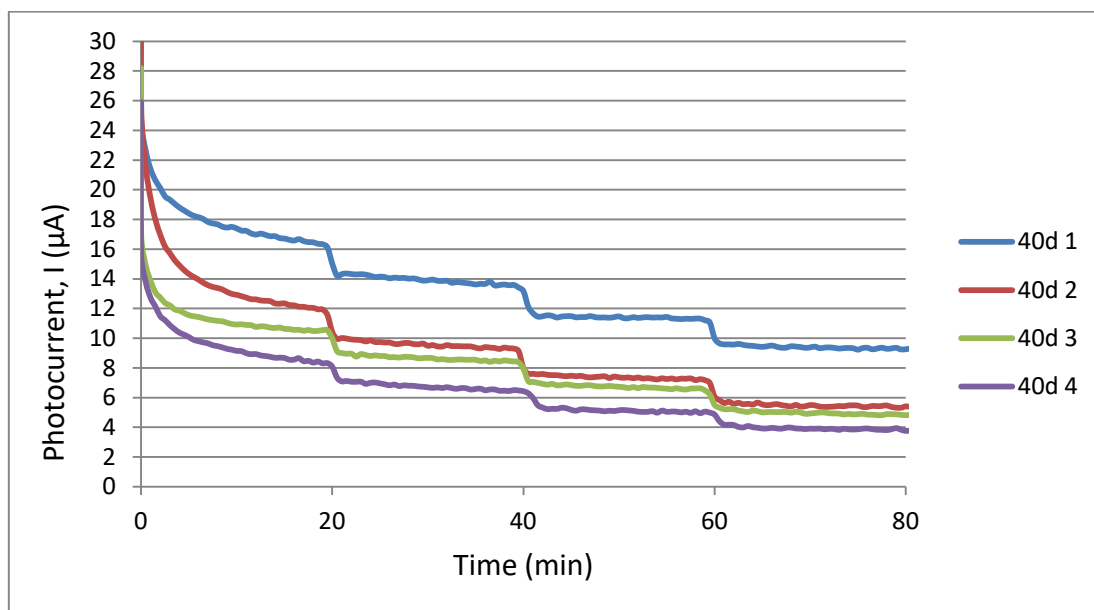
The samples (curves) of 40 $\mu\text{m}$  (wet and dry) are good. In the samples 55 $\mu\text{m}$  and 80 $\mu\text{m}$  apparently don't appreciate step down when the distance of the light change. For this, the graphics of the 55 and 80 are not worth.

Every change on the graphics, every step down, corresponds one intensity of ultraviolet light. Starting on 1.2, then 0.9, 0.6 and 0.3 mW/cm.

### 4.5.1. 40 $\mu$ m distances samples



**Figure 53.** Photocurrent measures of 40 $\mu$ m samples under water in front varying the distance of the ultraviolet light.

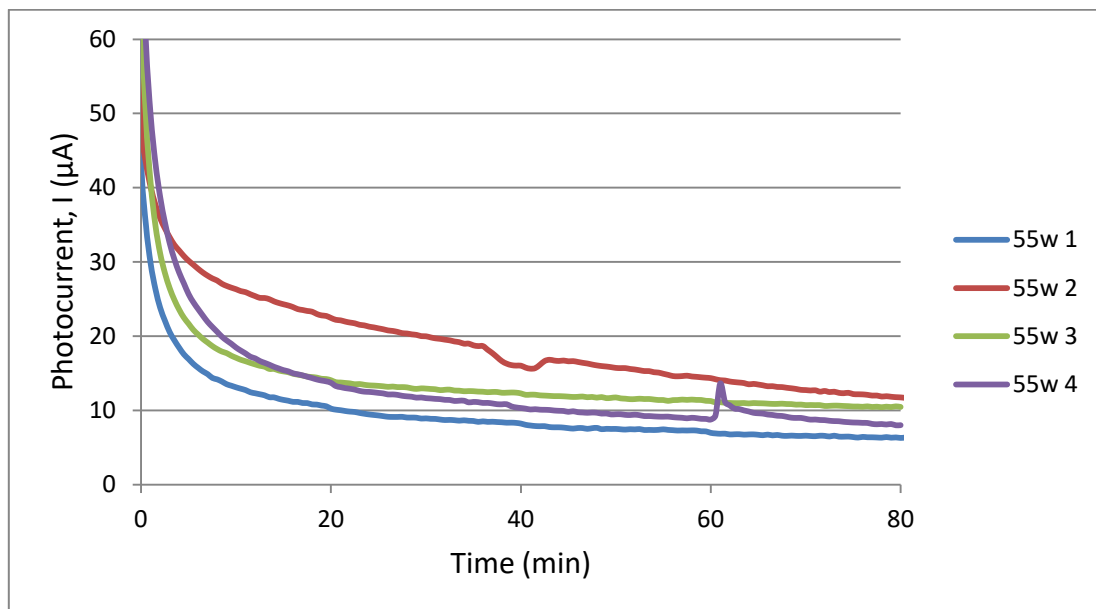


**Figure 54.** Photocurrent measures of 40 $\mu$ m samples on water in front varying the distance of the ultraviolet light.

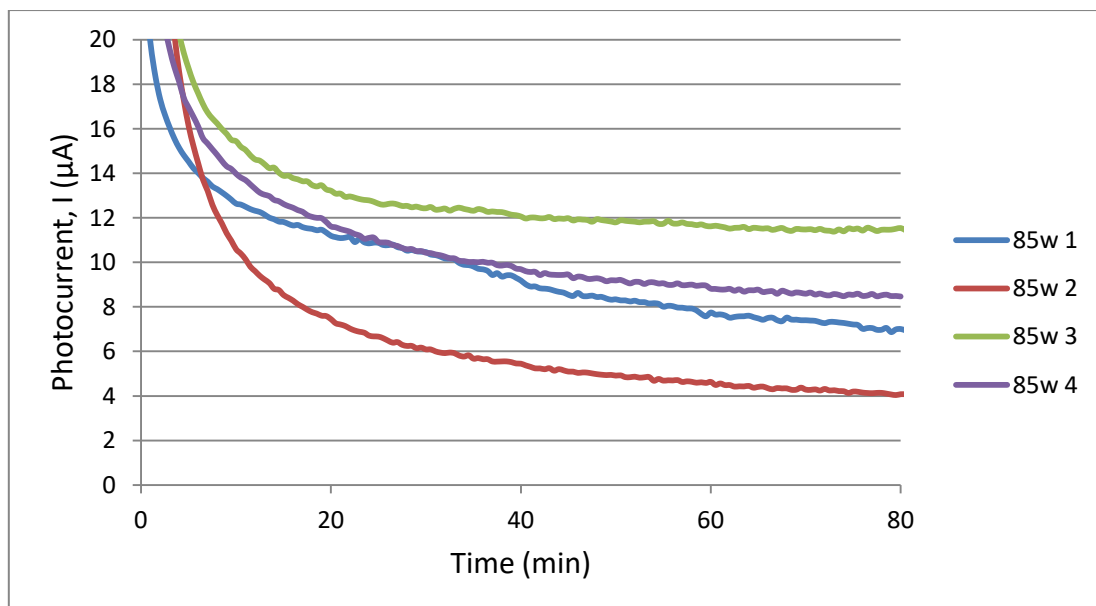
We see the difference on the 40 $\mu$ m wet samples (**Figure 53**) are smaller than the 40 $\mu$ m dry samples (**Figure 54**). Also, it gets higher values of intensities in every of the intensities of ultraviolet light.

#### 4.5.2. 55 $\mu\text{m}$ and 80 $\mu\text{m}$ distances samples

We have a problem with the 55 $\mu\text{m}$  and 80 $\mu\text{m}$  samples because their drops distances are so small, the difference when the light changes are very small, almost imperceptible, and the stabilization doesn't produce with the speed waited.



**Figure 55.** Photocurrent measures of 55 $\mu\text{m}$  samples under water in front varying the distance of the ultraviolet light.



**Figure 56.** Photocurrent measures of 80 $\mu\text{m}$  samples under water in front varying the distance of the ultraviolet light.

As we can observe, the steps down on the seconds 20, 40 and 60 doesn't appreciate with the same way than the 40 $\mu$ m distances samples (**Figure 53** and **Figure 54**). Also, the interferences produced in the result of the average of the intensities does the graphics are not worth.

#### 4.5.3. Photocurrent with glycerol in the electrolyte

We realize another normal amperometry with the samples 40 $\mu$ m wet but adding at the electrolyte of perchloric acid glycerol, 2%, 4% and 6% to confirm if there is an increment of the values in the amperometry with ultraviolet light. The best percentage of glycerol will be used for repeat the anterior test with the 55 $\mu$ m and 80 $\mu$ m distances samples.

When the graphs are observed we confirm the higher difference between the dark stabilized zone and the zone of the graphic with irradiation is when the electrolyte has a 6% of glycerol.

Then, this will be the percentage of glycerol chosen for do the test with the samples of 55 $\mu$ m and 80 $\mu$ m on step down to calculate the calibration graphics.

**Table 10.** Difference between the average when is the glycerol on the electrolyte and when not of sample 1.

Difference sample 1 ( $\mu$ A)	
0%	3,36E+00
2%	6,78E+00
4%	8,34E+00
6%	9,88E+00

**Table 11.** *Difference between the average when is the glycerol on the electrolyte and when not of sample 2.*

Difference sample 2 ( $\mu$ A)	
0%	9,79E+00
2%	6,07E+00
4%	7,55E+00
6%	8,46E+00

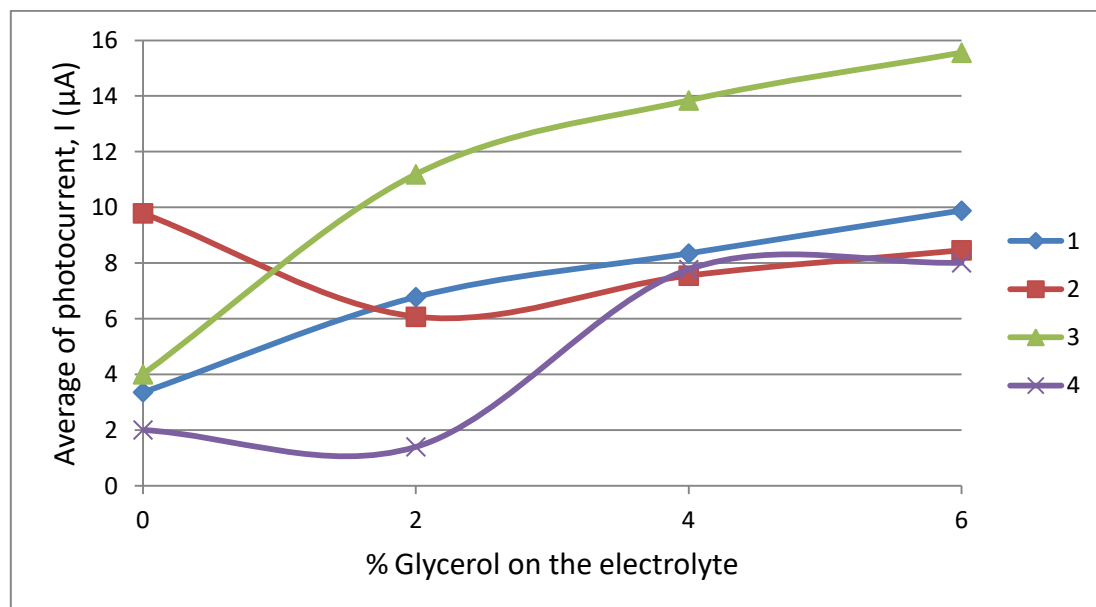
**Table 12.** *Difference between the average when is the glycerol on the electrolyte and when not of sample 3.*

Difference sample 3 ( $\mu\text{A}$ )	
0%	4,01E+00
2%	1,12E+01
4%	1,38E+01
6%	1,56E+01

**Table 13.** *Difference between the average when is the glycerol on the electrolyte and when not of sample 4.*

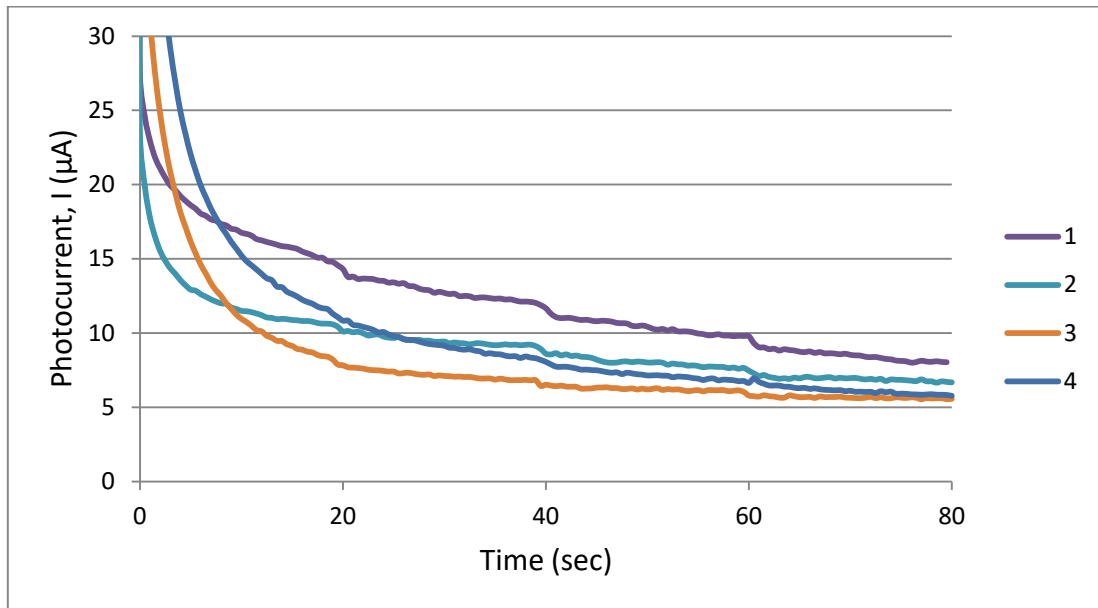
Difference sample 4 ( $\mu\text{A}$ )	
0%	2,48E+00
2%	6,51E+00
4%	8,17E+00
6%	8,85E+00

The **Figure 56** shows the difference of intensities between the stabilized averages when is the sample expose to the ultraviolet light and when not, in front the percentage of glycerol added at the electrolyte of four samples of  $40\mu\text{m}$  wet, treated previously 50 minutes.

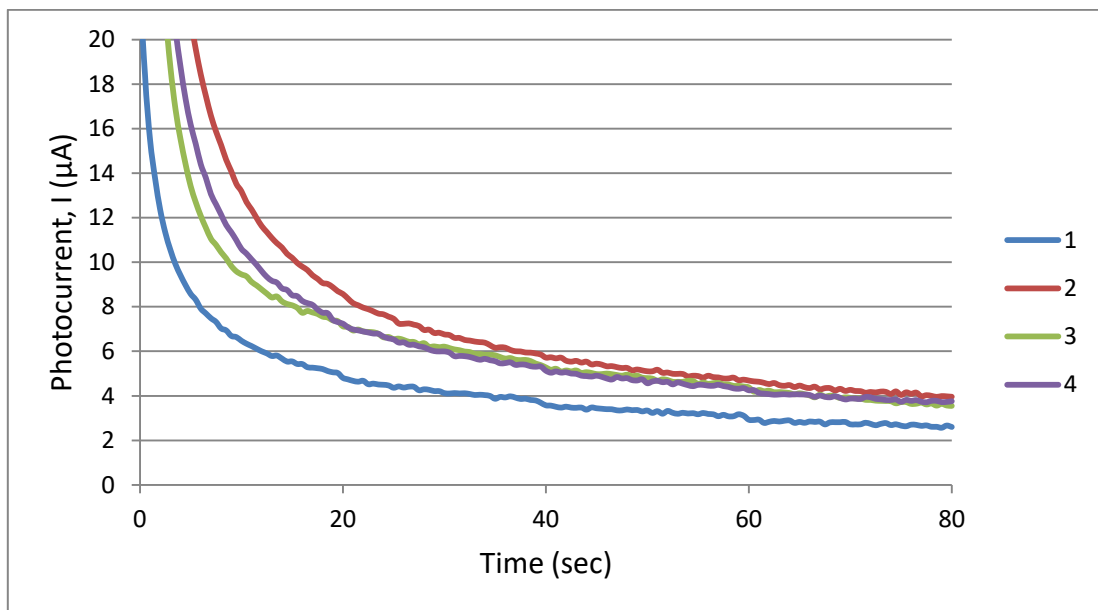


**Figure 57.** *Averages of photocurrent comparing with the % of glycerol in the electrolyte.*

We repeat the same test which we realized before, varying the distance of the light and, then, changing the intensity of the ultraviolet light for the 55 $\mu\text{m}$  and 80 $\mu\text{m}$  samples.



**Figure 58.** Photocurrent measures of 55 $\mu\text{m}$  samples under water in front varying the distance of the ultraviolet light with a 6% glycerol.

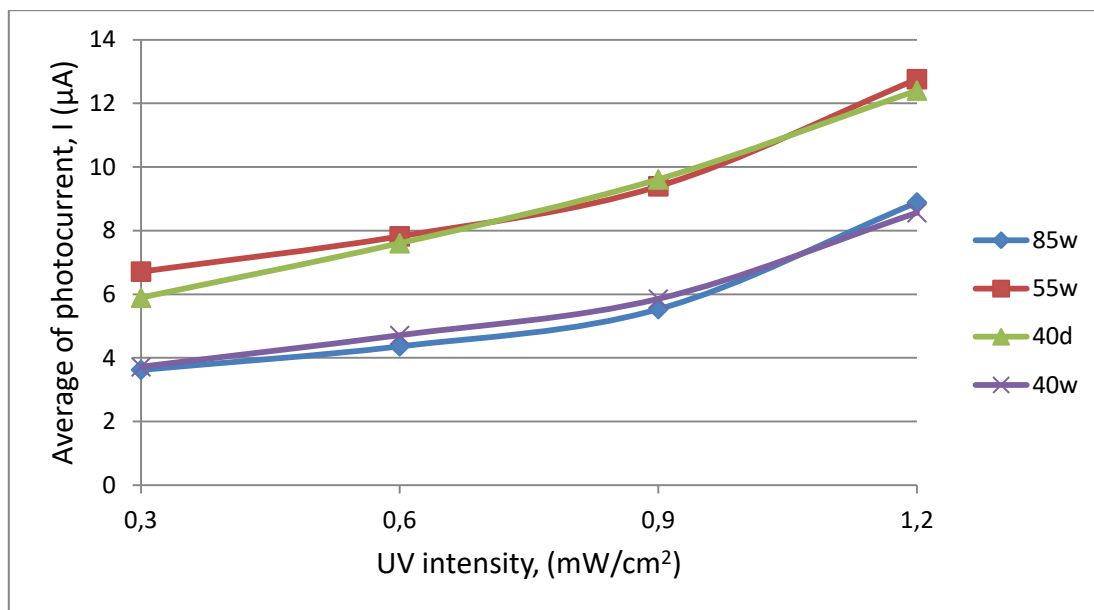


**Figure 59.** Photocurrent measures of 80 $\mu\text{m}$  samples under water in front varying the distance of the ultraviolet light with a 6% glycerol.

On the **Figure 59** the step down is very low when we vary the light. That's means we must add more glycerol to the electrolyte for get a result more specific, but we think this is enough to realize the calibration curve.

#### 4.6. Curve of calibration

In the **Figure 60** it can be seen the average of the samples while they were irradiated with different intensities of light, in front of the intensity irradiated.



**Figure 60.** Curves of calibration.



## 5. CONCLUSION

After the study realized about the sensors with different characteristics, and an observation of the graphics of the photocurrent we can say the better conditions for printing and treating the electrodes and do it like appropriated and sensitive sensors for the detection of the ultraviolet radiation are the sensors fabricated with the printing method with a distance between the drops of  $\text{TiO}_2$  of  $40\mu\text{m}$ . Not just this, also, the sensor has demonstrated have better properties and be more stable when the previous treatment of ultraviolet light for intertwine the molecules of  $\text{TiO}_2$ , the electrodes have been treated under the distillate water when they are under the ultraviolet lamp for do easier the kinetics. The electrodes with better results gotten were the ones that received the previous treatment for 50 minutes, although there is a difference between the results with the samples treated 30 and 50 minutes, this difference is not very high, and by this, not meaningful. Thanks to this, we can say when the samples are treated between this times we already obtain an appropriated sensor for the function which is going to be used.

Respect to the function which the sensor could be used, in this case the sensor with  $40\mu\text{m}$  and a previous treatment under water, the sensibility with a difference of 20mA if the light is inciting, or not, could be too much high, for that thanks to this study, we can get sensors that is going to adapted with the best way to our requirements and circumstances, varying the distance of the drops of  $\text{TiO}_2$  on the screen printing, the number of layers inks of the electrodes, the time of previous treatment and, also, the own ultraviolet light intensity.

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