UNIVERSIDAD SAN FRANCISCO DE QUITO USFQ

Colegio de Ciencias e Ingenierías

Design and Application of Low Cost Photoreactors for Applications in Photocatalytic Reactions

Roberto Rojas Cazar

Ingeniería Ambiental

Trabajo de integración curricular presentado como requisito
para la obtención del título de: Ingeniero Ambiental

Quito, 19 de diciembre de 2019

UNIVERSIDAD SAN FRANCISCO DE QUITO USFQ

COLEGIO DE CIENCIAS E INGENIERIAS

HOJA DE CALIFICACIÓN
DE TRABAJO DE INTEGRACION CURRICULAR

Design and Application of Low Cost Photoreactors for Applications in Photocatalytic Reactions

Roberto Rojas Cazar

Calificación:

Nombre del profesor, Título académico: Thomas Cadenbach, Ph.D.

Firma del profesor ______________________________

Quito, 19 de diciembre de 2019

Derechos de Autor

Firma del estudiante:	_______________________________________
Nombres y apellidos:	Roberto Rojas Cazar
Código:	00113929
Cédula de Identidad:	1104482466
Lugar y fecha:	Quito, 19 de diciembre de 2019

RESUMEN

Los procesos fotocatalíticos oxidativos se han estudiado en los últimos años, utilizando diferentes materiales fotocatalíticos y fuentes de luz. Uno de los objetivos principales es la degradación de contaminantes orgánicos peligrosos por fotocatálisis de semiconductores. En esta investigación actual exploramos la influencia de diferentes fuentes de luz necesarias para las reacciones fotocatalíticas. Aquí, presentamos una serie de foto reactores de bajo costo que requieren las características necesarias para lograr degradaciones óptimas de los tintes utilizados industrialmente. Se han estudiado varias fuentes de luz LED, por ejemplo, COB y LED de alta potencia. Además, se muestran los diferentes pasos para la construcción de un fotorreactor controlado Raspberry Pi que permite el control total de los parámetros espectrales, así como la monitorización de la temperatura y el pH durante los procesos fotocatalíticos. Una bomba peristáltica integrada permite una automatización completa de la reacción. Todos los reactores se evaluaron en la fotodegradación de Rhodamine B usando el fotocatalizador BiFeO3. Los resultados de las actividades fotocatalíticas han detectado que las fuentes que proporcionan luz azul / UV son las más eficientes en términos de eliminación de Rhodamina B, de acuerdo con los espectros de absorción. Por lo tanto, la fotocatálisis con BFO estándar y el fotorreactor Raspberry Pi de bajo costo se recomiendan para procesos de fotooxidación catalítica como un mecanismo prometedor para la degradación de los tintes de aguas residuales textiles.

Palabras Claves: Fotoreactor, Rhodamine B, Bismuto férrico, BiFeO3, Foto catálisis, Industria textil, Raspberry Pi, LEDs, COBs,

ABSTRACT

Oxidative photocatalytic processes have been studied in recent years, using different photo catalytic materials and light sources. One of the main objectives is the degradation of dangerous organic pollutants by semiconductor photocatalysis. In this present investigation we explore the influence of different light sources necessary for photocatalytic reactions. Here, we present a series of low-cost photo reactors that require the necessary characteristics to achieve optimal degradations of industrially used dyes. Various sources of LED light have been studied, for instance high power COBs and LEDs. In addition, the different steps for the construction of a Raspberry Pi controlled photo reactor that allows full control of spectral parameters as well as temperature and pH monitoring during the photo catalytic processes. An integrated peristaltic pump allows a full automation of the reaction. All reactors were evaluated in the photodegradation of Rhodamine B using BiFeO3 photocatalyst. The results of photo catalytic activities have detected that sources that provide blue /UV light are the most efficient in terms of Rhodamine B removal, according to absorption spectra. Thus, photo catalysis with standard BFO and the low cost Raspberry Pi Photo Reactor are recommended for catalytic photo oxidation processes as a promising mechanism for the degradation of textile wastewater dyes.

Keywords: Photoreactor, Rhodamine B, Bismuth Ferrite, BiFeO3, Photo catalysis, Textile industry, Raspberry Pi, LEDs, COBs.

TABLE OF CONTENT

LIST OF FIGURES

SUPPORTING INFORMATION

LIST OF TABLES

SUPPORTING INFORMATION

Design and Application of Low Cost Photoreactors for Applications in Photocatalytic Reactions

Roberto Rojas Cazar and Thomas T. Cadenbach

Universidad San Francisco de Quito, Departamento de Ingeniería Industrial, Colegio de Ciencias e Ingenierías "El Politécnico", Diego de Robles y Vía Interoceánica, Quito, Ecuador

ARTÍCLE INFORMATION:

Artícle Hisory:

Keywords:
Photoreactor,
Rhodamine B,
Bismuth Ferrite, BiFeO3
Photocatalysis
Textile industry
Raspberry Pi
LED

ABSTRACT

Oxidative photo catalytic processes have been studied in recent years, using different photo catalytic materials and light sources. One of the main objectives is the degradation of dangerous organic pollutants by semiconductor photocatalysis. In this present investigation we explore the influence of different light sources necessary for photocatalytic reactions. Here, we present a series of low-cost photo reactors that require the necessary characteristics to achieve optimal degradations of industrially used dyes. Various sources of LED light have been studied, for instance high power COBs and LEDs. In addition, the different steps for the construction of a Raspberry Pi controlled photo reactor that allows full control of spectral parameters as well as temperature and pH monitoring during the photo catalytic processes. An integrated peristaltic pump allows a full automation of the reaction. All reactors were evaluated in the photodegradation of Rhodamine B using BiFeO3 photocatalyst. The results of photo catalytic activities have detected that sources that provide blue /UV light are the most efficient in terms of Rhodamine B removal, according to absorption spectra. Thus, photo catalysis with standard BFO and the low cost Raspberry Pi Photo Reactor are recommended for catalytic photo oxidation processes as a promising mechanism for the degradation of textile wastewater dyes.

Introduction

Pollution due to modern industrial activities, population growth and long-term droughts have caused a shortage in clean water sources, in consequence water has become one of the most precious resources and its conservation is one of the most important challenges that humanity is facing right now. Due to the high demand for clean water for the world population several strategies, practices and solutions have been developed to increase the supply of viable water sources (Chong, 2010). Research and development in technological fields for the conservation of natural resources is necessary for the preservation of water systems affected by anthropogenic activities.

One of the highest polluting industries is the textile industry. Textile industries represent a sector of great importance in the world economy, especially in developing countries. Among the variety of pollutants discharged, it is possible to find heavy metals, emerging pollutants (persistent organic compounds, endocrine disruptors, antibiotics), hydrocarbons, organic matter, and compounds that produce coloring in effluents (Deblonde, Cossu-Leguille and Hartemann, 2011). Textile dyes are compounds of high concern because they generate negative impacts on water systems, several of these organic compounds are considered carcinogenic, toxic and mutagenic (Torres-Luna et al, 2016).

In Ecuador, the textile industry represents 8% of the Gross Domestic Product (GDP) and is considered the second sector with the highest employment contribution in the country (Ministry of Industry and Productivity, 2016). Consequently, it is necessary that new, adequate and efficient technologies be acquired by industrial sectors for their water treatment processes. One of the processes by which water cleaning can be achieved is through Advanced Oxidation Processes (AOP).

AOPs have advantageous characteristics compared to traditional methods, such as lower generation of by-products, lower toxicological effects, treatment of pollutants in low concentrations, and lower sludge formation.

One example of an AOP is photocatalysis, especially photocatalytic reactions using visible light semiconductors (Urkiaga et al., 2011). Photocatalytic reactions produce electron holes and excited electrons that participate in different oxidation-reduction reactions that result in the formation of highly strong oxidants such as the hydroxyl radical (OH^*) and anions such as peroxide ($O_2^{¿-¿¿}$) (Schneider, et al., 2014), which are responsible for the mineralization of organic compounds (Khademalrasoola, 2016).

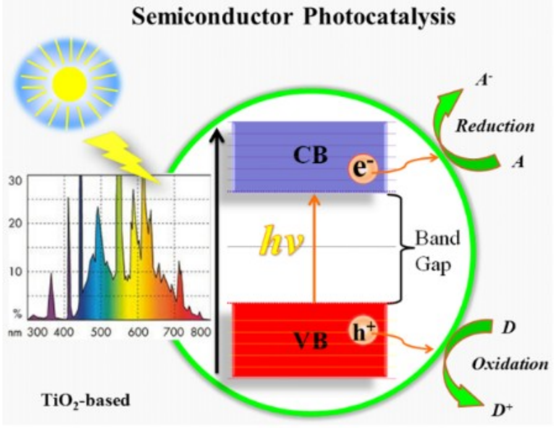


Figure 1. Mechanism of photo induced formation of electrons in a semiconductor photo catalyst with presence of organic contaminant Image: (Tianjin University of Technology, 2018)

Photocatalytic degradation processes occur when a semiconductor is subjected to adequate light sources. These provide an amount of energy greater or equal to the band gaps of the semiconductor material, thus the electrons of the photo catalyst are activated (excited) and they move from the valence band to the conduction band Eq. (1).

Consequently, electron holes ($h^{+\text{¿}\text{¿}}$) are created to react with H_2O and produce oxidizing radicals OH*, Eq. (2) these strong oxidizing radicals react with the dye (organic pollutant) to produce $CO_2 \wedge H_2O$, Eq (3). Afterwards other reactions could take place in the recombination of electrons and holes generating heat Eq. (4) that could affect the photo catalytic activity (Schneider, et al., 2014). Also, the excited electrons can react with O_2 to produce superoxide anions $O_2^{\text{¿}-\text{¿}\text{¿}}$, Eq. (5) (Mamun, Kurny, & Gulshan, 2017). The reaction involved in the photo degradation is shown below:

$$Catalyst+hv \rightarrow e_{CB}^{-\text{¿}+h_{VB}^{+\text{¿}\text{¿}}\text{¿}} \qquad (1)$$

$$h_{VB}^{+\text{¿}+OH^{-\text{¿}(surface)\rightarrow OH^{\text{¿}}\text{¿}}\text{¿}} \qquad (2)$$

$$OH^{\text{¿}}+Dye \rightarrow CO_2+H_2O \qquad (3)$$

$$e_{CB}^{-\text{¿}+h_{VB}^{+\text{¿}\rightarrow Heat\,\text{¿}}\text{¿}} \qquad (4)$$

$$e_{CB}^{-\text{¿}+O_2\rightarrow O_2^{\text{¿}-\text{¿}\text{¿}}\text{¿}} \qquad (5)$$

Heterogenous photocatalysis employing different semiconductor catalysts (TiO_2,ZnO,CdS,ZnS) has shown its efficiency in the degradation of plenty of refractory organics into readily biodegradable compounds. Among these catalysts titanium dioxide (TiO_2) has gotten important attention in photocatalysis technology due to its chemical and thermal making it the most commonly used semiconductor in photocatalytic water treatment (Chong, 2010). However, as it has a band gap of 3.2 eV only UV light (300-390 nm) can be used for its activation. In consequence, he synthesis of new catalysts that work in visible light ranges is necessary.

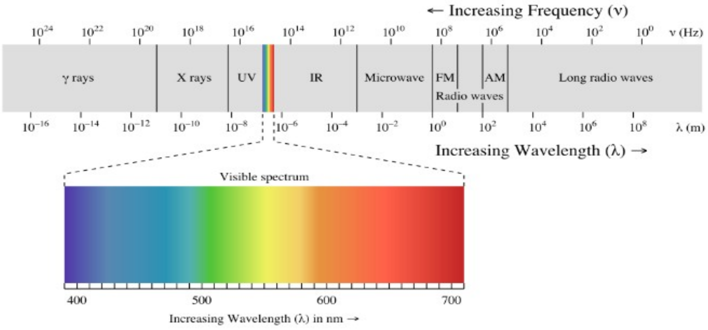


Figure 2. Electromagnetic waves spectra, and the range of visible light. Image: (Quora, 2019)

In recent studies, BiFeO3 has proven to be a quality semiconductor catalyst in the remediation of wastewater effluents such as oxidation of organic pollutants and degradation of dyes mainly due to its narrow band gap (2.2 eV), high chemical stability and the generation of its own electric field that induce the separation of photogenerated electron-hole pairs within its structure (Teng, et al., 2013).One of the main elements for obtaining successful photo catalytic processes is the design of reactors that provide the energy necessary for the activation of catalyst surfaces.

Traditionally, ultraviolet lamps have been used for this purposes, UV lamps are electric discharge lamps that emit lshortwave UVA radiation and a short region of visible light (320-400 nm), also mercury lamps (Blue 436 nm, Green 546 nm, Yellow-Orange 578 nm), and xenon lamps that produces a bright white light with a peak in 468 nm, among others. Some inconveniences related to their cost, maintenance, fixed wavelength, fragility, internal gas leaks, danger of explosion, and the high toxicity of the gases are present.

In addition, the life time of these light sources is 500-2000 hours which work at high temperatures making heat dissipation difficult in these systems by presenting a high energy consumption (Khademalrasoola, 2016). A relatively new light source is the LED light (Light Emitting Diode), which has distinct advantages compared to traditional light sources such as low power consumption, life time (25000-100000 hours), physical protection, reduced size, and affordable prices(Volatier, 2010),also an important advantage is their emission of very precise spectrum with sharp spectral bandwidths.

Table 1: Main characteristics of the traditional light sources.

Light sources	**Price ($)**	**Power Supply ($)**	**Lifetime (h)**
UV lamps	200	500-4000	200-5000
Mercury lamps	80	2000-6000	200-5000
Xenon lamps	700	200-1500	200-3000
Tungsten lamps	60	250-1500	200-3000

In recent studies, near UV LEDs with a wavelength of 385 nm were used in water and air purification processes (Jhonson, 2003) , moreover, a series circuit with 16UV-LEDs with a wavelength of 375 nm was used in the photocatalysis oxidation of perchloroethylene, Also, photoreactors that use LEDs that emit visible light such as blue, red, green or white light have been used as light sources for different photocatalytic processes (Khademalrasoola, 2016). Within the degradation experiments it is very important that the temperature does not interfere with the photodegradation reactions that are occurring in the system. Two different sources of temperature could affect the photocatalytic degradation of the dye, the reaction temperature and the light source temperature. The reaction temperature is referred to the heat that could be produced by the recombination of excited electrons and electron holes within the solution. Various studies have been carried out regarding the dependence of the reaction temperature on photocatalytic activity (Muradov et al., 1996; Fu et al., 1996; Chen and Ray, 1998; Rincon and Pulgarin, 2003; Evgenidou et al., 2005). Although these measurements have been made in photo catalytic activities using a different catalyst than in this research (TiO2), it has been shown that thermal energy in the form of temperature exceeding 80 ℃ promotes the recombination of charge carriers and does not help the activation of the surfaces of the catalysts, causing an incorrect adsorption of the organic compounds (Gaya and Abdullah, 2008). On the other hand, the light source temperature is referred as the heat created by the light source that is being used in the reactor. Each light source generates a different temperature, according to Wien's physical displacement law, there is an inverse relationship between the wavelength to the emission peak of a black body and its temperature::

$$\lambda_{max}=\frac{0.0028976\,m.K}{T}(6)$$

Where T is the temperature of the black body in Kelvin (K) and λ_{max} the wavelength of the emission peak in meters (m) and the Wien’s constant (K.m), which states that while the temperature of a black body is higher, its emitted wavelength will be shorter.Therefore, the internal heat of the reactor will increase depending on the light source that is being used. It is important to notice that both of these sources of heat affect tbe temperature of the solution and the mineralization of the dye. In consequence, the addition of an efficient cooling systems is crucial in the construction of photoreactors.

The use of visible and UV light, in addition, to the commercialization of low-cost and high-voltage LEDs has allowed photo-reduction catalysis reactions to be highly used and built on an academic level. Likewise, much attention has been given to improving degradation rates by standardizing operating protocols (Chi Le, 2017). There are a handful of researchers who have developed photo reactors for degradation processes which differ mainly in their technical characteristics for their operation, that is, the amount of light needed, the amount of LEDs, their color, the proximity of the sample to the light source, the geometric shape of the reactor, ease of use and its energy efficiency (Khademalrasool, 2016, Katic, et al., 2018, Sergey, 2015, Cadenbach, 2017).

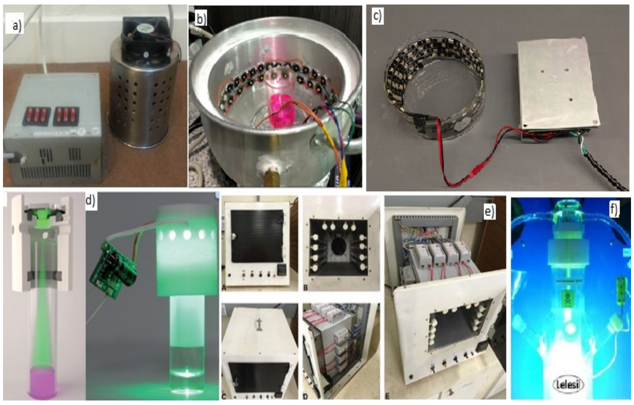


Figure 3. DIY photoreactors constructed in recent studies.
a) (Khademalrasoola, 2016) b) (Cadenbach, 2018) c) (MacMillan Group Princenton) d) (Sergey, 2015) e) Katic, et al., 2018 f) (Lelesil)

However, photoreactors that have been created in recent years belong to two different groups, the Do It Yourself (DIY) reactors and the Commercially Available Photoreactors (CAP). The DIY photo reactors combine high power LEDs, and cooling systems in one device. On the other hand,the CAP reactors present more features such as temperature sensors, modular light sources and a stirring function, such as the Penn OC Photoreactor developed by the MacMillan Group at Princeton University and Merck & Co., Inc. however, it is considered a very limited reactor still at a high price. A significant difference between these reactors are their prices, where the low cost ones are the DIY reactors (depending on the light source used) while the CAP reactors present higher prices that can go up to tens of thousands of dollars. For instance, the Pennoc OC M2 cost around $6200 plus $900 for the light source. Although this reactor is considered high quality, the light sources used are found in the market for much lower values ($6-15) . Due to this, it is sought to build a photoreactor that outperforms the existing DIY and CAP photoreactors offering higher functionalities and other features. These features include a fully custimozable modular design, full control of spectral wavelength and intensity, active colling, magnetic stirring with speed control, pH monitoring, temperature monitoring, dosing pumps for an optional/separate autosampling unit, a touch screen control (7'' screen with resolution of 800x480 pixels) controlled by a Rasppberry Pi. Consequently, in the present research work the performance of each light source and reactor was tested in visible light degradation photo reactions of the organic dye Rhodamine B using BiFeO3 as a semiconductor photo catalyst.

Design and Construction of Photoreactors

COB Photoreactor

For the construction of the first reactor, different Chanzon and Cree Chip on Board (COB) light sources with different features and temperatures wereused. These light sources will have the same configuration for their operation, where a 15 cm diameter, 17.5 cm high Al structure was used. The required voltage is 30-34V and a current of 3A for the Chanzon and the Cree COBs, which uses a Mean Well SE-350-48 power supply with an AC-100-120V / 7.0A voltage input and a DC-48V / 7.3A output, in addition a Drok DC-DC voltage converter with a 10-75V input and a 0-60V output. Also 3 fans were added to achieve cooling.

Figure 4. Configuration of the COB Photoreactor

LED Photoreactors

12 LEDS Photoreactor

The construction of this reactor consists of an electrical circuit of Cree LEDs that are connected in series within four heat sinks. This reactor contains 12 LEDs, which are divided by 3 for each side of the heatsink, and different colors were placed to achieve a wide wavelength within the visible light spectrum. The size of the structure is 9.5 x 7.1 x 3.4 cm and it is composed of aluminum, with the aim of maintaining the reactor temperature an 8 cm diameter fan has been used. The power source for this reactor is a Mean Well LPC-35-700 with an AC input of 100-240V / 1.1A and a direct current output of 48V / 0.7A.

Figure 5. Configuration of the 12 LEDS Photoreactor

6 ROYAL BLUE LEDS Photoreactor

The construction of the following reactor consists of an electrical circuit of Cree LEDs that will be connected in series within a circular structure. This reactor contains 6 Royal Blue color LEDs. The dimension of the structure is 16 cm high and 13 cm in diameter. and is composed of aluminum. The power source for this reactor is Mean Well LPC-35-700 with an AC input of 100-240V / 1.1A and a direct current output of 48V / 0.7A.

Figure 6. Configuration of the Royal blue LEDs Photoreactor

44 LEDS – AL POT Photoreactor

For this research a previously built photoreactor will be used as a second reference (Santillan, 2018). The reactor consists of an electrical circuit of Cree LEDs that will be connected in series within a circular structure. This reactor contains 44 High Power LEDS, mainly White, Blue and UV LEDS. It has a water-cooling system within its structure. The dimension of the structure is 13 cm high and 20 cm diameter. and is composed of aluminum. The power source for this reactor is 2 Mean Well LPC 35-700 power supplies with an AC input of 100-240V / 1.1A and a direct current output of 48V / 0.7A. and one Mean Well LPC-60-14000 with an AC input of 100-240V / 1.2A and a direct current output of 48V / 1.2A.

Figure 7. Configuration of the 44 LEDs Photoreactor

Reference Light Source

KESSIL Tuna Blue

For the configuration of this reactor an aluminium circular structure with a diameter of 10 cm is used, it is also covered with aluminum foil to increase the reflection of the present light. This light source has its own cooling and a system to control the intensity and spectrum (Tuna Blue 10000-12000K and Tuna Sun 6000-9000K), it also has a 24V/5A power supply. The light is attached to a mechanical arm that will allow to control the distance of the light source to the sample. For the stirring function a stirring plate was used as observed in Fig 8.

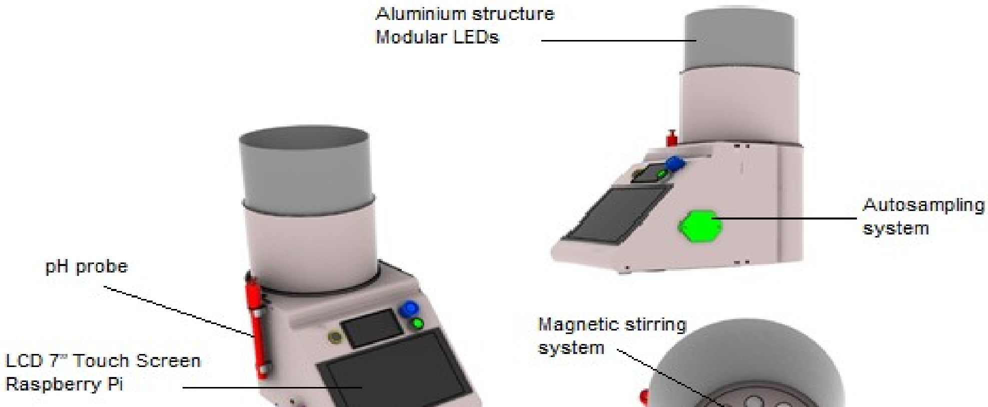
Figure 8. Configuration of the KESSIL BLUE Photoreactor

RASPBERRY PI Photoreactor

The Raspberry PI controller is a low cost free software computer board that by operating Linux-based operating systems allows the loading of several free access programs. In addition, Raspberry Pi also contains electronic devices such as temperature, light, motion, acceleration, pressure sensors controlled through its GPIO (General Purpose Input / Output), UART (Universal Asynchronous Receiver-Transmitter), and SPI (Serial Peripheral Interface), I²C (Inter-Integrated Circuit) pins. The Photoreactor uses a software called Reef-pi created by Ranjib Dey, it is a reef aquarium controller based on Raspberry Pi. Although the main objective of Reef-Pi is to automate reef aquariums, it can be useful controlling general purpose equipment. It is a modular controller and can be configured to execute a set of functions, the driver software runs on Raspberry Pi and uses complementary electronic components for all its functions: LED light control by dimming, temperature control with an alert if it exceeds the specified temperature range, autosampling using the dosing functionality by reversing the pump direction and withdrawing the sample, continuous pH monitoring of the sample. The Electronic components that are going to be needed are a Raspberry Pi 3 Model B +, a Perma-Proto Board Pi HAT Adafruit, female and male jumper cables, female and male pins, Rasperry Pi. Touch Screen LCD 7’’ and a 32 Gb SD Card. For a more detailed installation and configuration of the Reef-Pi software and the electronic features see Support Information*.

LED Intensity and Spectrum controller. –

For the light controlling at first a cylindrical aluminium structure with a diameter of 17 cm was used. Within the structure seven channels of different high power Cree LEDs in different colors are connected in series, each LED was secured with two screws and thermal paste was also added, all the LEDs are mounted with 60 degree lenses. The colors used are 4 Royal Blue, 4 Cool White, 2 Warm White, 2 Red, 2 Green and 7 UV in 3 different wavelengths. The voltage an amperage needed for each LED are Blue and White (3V, 1.5A), Red and Green (3V, 1 A), and UV (2.8V, 700 mA). For each channel a proper driver was used and connected to a 16-channel Pulse Width Modulation (PWM) PCA9685 Servo Driver, this component will be connected via I2C to the Raspberry Pi using a Perma Proto Pi HAT board trough a VCC 5V pin, a GND pin and SDA/SCL pins for the transmission of data.



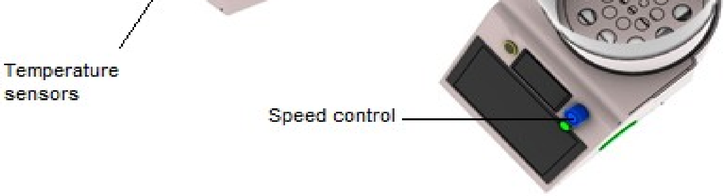


Figure 9. Configuration of the Raspberry Pi Photoreactor

The PWM allows cycle of a periodic signal on a very small amount of time (approximately 1/500 of a second), it is useful to communicate with an analog form with digital systems. This communication is allowed by an analog/digital converter that will measure the duration of the cycle of a specific tension in a digital way, for example, 0V and 5V as digital values of 0 and 1 (0-100% duty cycle), if the output is 5V for 90% of the time, the load will get 90% of the power delivered to it. The servo drivers are controlled by PWM where their position is modified accordingly to the width of the pulse that is sent to in a certain period (Barr, 2001). The Reef-pi software allows the digital control of the intensity of the LEDs for each channel, on the contrary a potentiometer would have changed the color of the LEDs.

Temperature Sensors. -

The temperature monitoring system works with a DS18B20 submergible sensor, this sensor is connected to the Raspberry Pi trough a VCC 3V pin, an GND pin and the GPIO #4 pin for data. A 4.7K resistor is needed between the power and data connection. The pins are connected to a 3.5 mm female audio jack and the sensor is configured with the male connection. Within the configuration of the temperature monitoring you can choose the name of the sensor, the unit of measurement and also an alert if required.

pH meter. -

For the construction of this device it is necessary to build a circuit that interacts with the SDA and SCL openings of the PermaProto HAT mint board, which will be connected to the EZO Atlas Scientific circuit together with a 5V and GND input, in addition, it is necessary to place two resistors 4.7K on the SDA and SCL data connections. This will be connected to an Atlas Scientific probe that will measure the pH of the solution. For the configuration in the reef-pi software, the probe is recognized where you can choose the frequency of data taking, the alerts and the calibration using the calibration solutions in the midpoint (pH 7), the low point (pH 4) and the highpoint (pH 10). The pH measurements are an important feature in the photoreactor because it helps us monitoring this value, allowing the user to control it and don't affect the reactions.

Autosampling system. –

For the configuration of the sampling automation system a peristaltic pump is connected to the Perma proto Pi HAT, this pump based on DC motors are connected to a L293D IC. The PWM pins from the Raspberry Pi are connected to the L293D, also the pins for the direction and velocity, two ground and a voltage converter from the 12V needed in the pump to 5V required to power all the system. This power supply will power the entire Photoreactor. For the configuration of the pump a calibration is needed, here you can choose the volume of sample that the pump must take in a desired time. This calibration is achieved by putting the speed and time in the reef-pi options.

Cooling and stirring system. -

The cooling and stirring system is constructed with an Arctic fan, Nd magnets and a PWM Motor Speed Controller DC Display Switch 6-30V 8A. Also we need a 12V power supply, for this the LDD drivers that has a 12V input within the same drivers are used. With this device it will be able to control the speed of the stirring system and will allow the reactor the cooling that is needed. Here the Nd magnets are placed in the fan, the fan is connected to the velocity controller, this velocity controller is connected to the 12V input in the LDD Drivers of the lights and the On/Off switch. This feature allows the sample to have a complete magnetic agitation during the photocatalysis process.

3D Design and Assembly.

Once all the electronic circuits are built, it is necessary to assemble everything in a structure that will allow all the components come together in one photo reactor. For this the design must be accurately constructed, also the material of the reactor will have excellent strength and temperature resistance. For this, the material used is polycarbonate that will be 3D printed in pieces that will be assembled with all the electronic components inside. The most common material for 3D printing is PLA, however, this material has a low temperature resistance (<70°C), where after some tests the material would change its shape in contact with the aluminum structure. The polycarbonate offers us a great mechanical and temperature resistance (>95°C) as it is mainly used in engineering applications.

Figure 10. Raspberry Pi Photoreactor

Light sources spectra measurements

Photocatalytic processes depend on the type and intensity of the light that will be used, it is important to characterize every light source in depth. Every semiconductor needs the right amount of energy for its activation. For instance, TiO2 photocatalysis requires UV light whereas BFO based catalysts require visible light sources. For the measurement of the spectra, the AvaSpec Sensline Avantes spectrophotometer belonging to EMA-USFQ (Atmospheric Measurement Station) was used.

As observed in the Fig.11 the spectral wavelength of the light sources that will be placed in the COB photoreactor are characterized. These light sources provide a significant coverage of the visible spectrum where its wavelength peaks in the Blue (450nm) and White-Yellow (550 nm) region for all the light sources where the CH6000K show a lower intensity in this region.

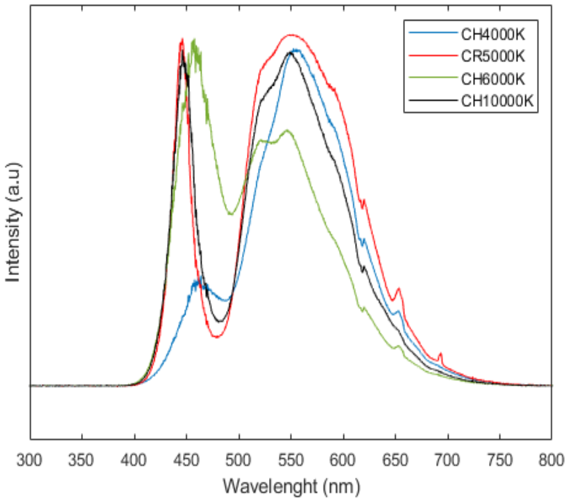


Figure 11. Spectral wavelength of the COB light source

In the Fig.12 the spectral wavelength of the LED Photoreactors are shown. These photoreactors provide a significant coverage of the visble spectrum where its wavelength peaks in the Blue (450nm) for the 6 Blue LED, and the 12 LED and 44 LED photoreactors in the White-Yellow (550 nm) with a part in the Blue/UV region.

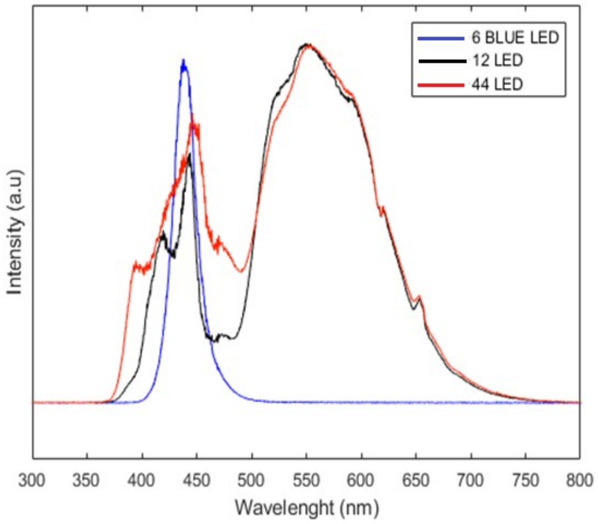


Figure 12. Spectral wavelength of the LED reactors

As observed in the Fig. 13 the spectral wavelength of the reference light sources are characterized, where the intensity of the lights were dimmed.by 50% for each case. These light sources provide a significant coverage of the visible spectrum where its wavelength peaks in the Blue (450nm) and White-Yellow (550 nm) region for the Kessil Tuna Sun, and for the Kessil Tuna Blue a dominant peak at the Blue region and also a significant peak in the UV region, that might help in photocatalytic processes.

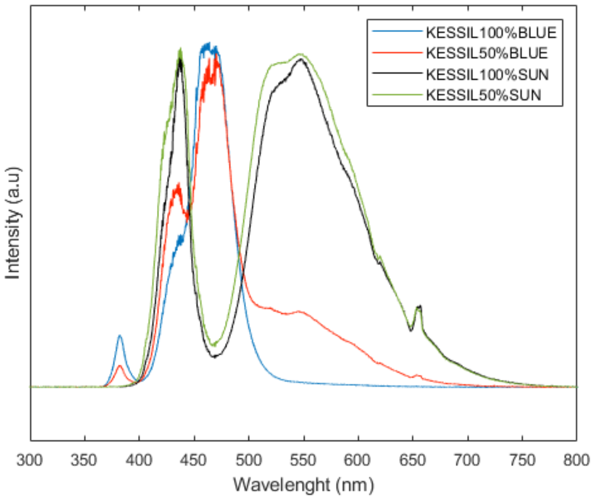


Figure 13. Spectral wavelength of the reference light sources

In the Fig.14 the spectral wavelength of the light sources that are placed in the Raspberry Pi photoreactor are characterized. These light sources provide a significant coverage of the visible spectrum where its wavelength shows peaks in the close to the Blue (450nm) region. The wavelength of this reactor is completely customizable where the intensity is changed as required for the activation of the semiconductor.

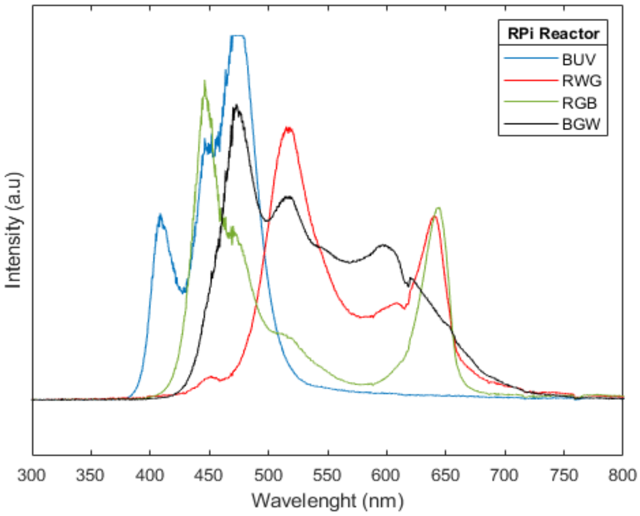


Figure 14. Spectral wavelength of the RPi reactor

Temperature Behavior

The temperature behavior experiments were carried out by taking data for each light source in an interval of 30 minutes, with the help of the temperature sensor incorporated in the stirring and hot plate. The temperature is an important feature to measure in photocatalytic processes because it can intercede in the photodegradation of the dyes. The measurements were done with all the light sources used, where at first the addition of 3 fans was analyzed showing a decrease of 2° C in the internal temperature of the COB reactor, this helped us to understand the dependence of the temperature of these reactions.

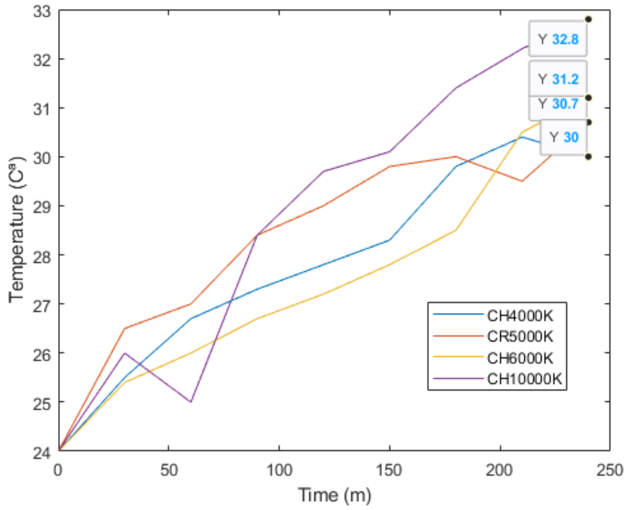


Figure 15. Temperature behavior of the COB light sources

As observed in the Fig 15. the temperature behavior of the COB LEDs is shown, where the CH4000K showed the lowest value 30° C, the CR5000K reached a value of 30.7° C, the CH600K showed a maximum value after 4 hours of 31.2° C, and the highest value belongs to the CH1000K with a value of 32.8° C. It is important to mention that these measurements were made with the 3 fans placed in the COB structure. For the LED photoreactors the 6 Blue LED showed the lowest value 30.2° C, the 12 LED reached a value of 31.1° C, and the 44 LED showed the highest value after 4 hours of 31.7° C. In the case of the reference light sources, the Kessil Tuna Blue reached a temperature of 32.5° C and the Kessil Tuna Sun reaches a value of 31.6° C, the Raspberry Pi photoreactor had the highest temperature with a value of 45° C All the graphics for the temperature behavior are found in Support Information*.

Light intensity measurements

The measurements of the light intensity are taken analyzing the real and non-subjective illuminance of an environment of each light source used, the instrument works in terms of Lux (lx), which by means of photoelectric cells capture the energy in the form of light transforming them into electrical impulses (Lighting Industry Federation,1994), Where:

$$1\,lx = 1\,lm/m^2 = 1\,cd.\,sr/m^2 \qquad (7)$$

The lumen (lm) is the unit that measures the luminous flux of a light source and is equal to a candle (the elementary unit of light) by a steradian (the solid angle subtended at the center of a unit sphere by a unit area on its surface) that measures the solid angles (the amount of the field of view from some particular point that a given object covers) of the surfaces that are illuminated. (Walsh, s.f). The sensor of the instrument must be located at 1 meter from the light source to be taken correctly, due to the formation of the solid angle that will be measured of each light source. This measurement is important because the luminous flux can ahow us the amount of photons that would reach the sample.

Table 2: Light intensity values of the LED photoreactors

Light Source	Lumen/m2
44 LED REACTOR	10346
12 LED REACTOR	7875
6 BLUE LED REACTOR	8279

In Table 2. the luminous flux values are shown for the LED photoreactors were the 44 LED reactor show a value of 10346 lx, also the 6 Blue LED reactor a value of 8279 lx and the 12 LED reactor with the lowest value of 7875 lx. The results for the light sources in the COB photoreactor, the reference light sources and the Raspberry Pi photoreactor are shown in the Support Information* section.

Synthesis of Bismuth Ferrite (BiFeO3)

The reagents used for the synthesis are bismuth nitrate pentahydrate $(Bi(NO_3)¿¿3.5H_2O)¿$, ferric nitrate $(Fe(NO_3)¿¿3.9H_2O)¿$and tartaric acid $(C¿¿4H¿¿6O_6)¿¿$, dissolved together with the methoxyethanol $(C_3H¿¿8O_2)¿$ and nitric acid (HNO_3), then the solution is stirred for 1 hour at room temperature. The solution is taken to the rotary evaporator at a temperature of 75 ° C for 1 hour, then dried at 75 ° C in the oven for 3 hours, it is crushed in a quartz bowl and then calcined with a 25 ° C ramp at a rate of 1 ° C/min up to 200 ° C for two hours, then at a rate of 1 ° C/min up to 250 ° C for 2 hours and finally 550 ° C for 1 hour at a rate of 4 ° C/min (Morales, 2019).

Evaluation of Photocatalytic Activity

The photo catalytic activity of the samples is developed and analyzed based on the photo catalytic degradation of Rhodamine B (RhB) under the visible light of each reactor. An absorbance calibration curve for Rhodamine B is obtained by preparing a stock solution of 5 mg /L RhB, then measuring the absorbance at different dilute concentrations. By means of this curve a calibration curve is obtained that will serve to obtain the concentration present in the sample. The absorbance is measured in the spectrophotometer by scanning between 400-1100 nm, where the intensity of the RhB absorption peak (554 nm) is directly proportional to the concentration of the dye, which is represented by the Beer- Lambert equation (Harris, 2010):

$$A = \log_{10}\frac{I_o}{I} = \varepsilon\, l\, c \qquad (8)$$

where, A is the light absorption by the sample, I is the intensity of light passing through the sample, Io is the initial light intensity, ε is the molar absorbance coefficient of wavelength ($M^{-1}cm^{-1}¿$, l is the path length (cm) and c is the concentration of the sample (M). In Figure 16, the calibration curve obtained for the concentration of RhB is observed.

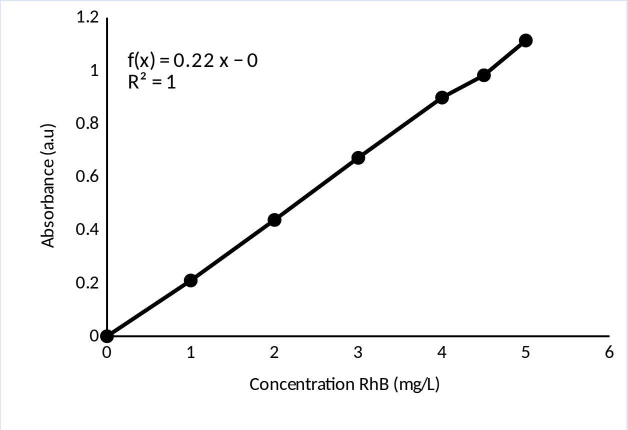


Figure 16. Rhodamine B calibration curve

Experimental tests for degradation are carried out in a 100 ml beaker containing 50 mg of standard BFO together with 50 ml of the 5mg/L RhB solution.

In order to have a homogeneous solution and achieve a balance of absorption-desorption between the photo catalyst and the dye the sample is stirred for one hour without the influence of any light source. Then the sample is measure the first sample and after 4 hours to obtain the last sample, the sample must be centrifuged at a speed of 6000 rpm for 1 minute in order to separate the catalyst powder from the solution. The maximum intensity of the absorbance peak of the RhB is measured with the help of the GENESYS 30 spectrophotometer. For each sample, the corresponding final RhB concentration is obtained using the standard RhB curve and the maximum absorption peak.

Results and Discussion

Characteristics comparison of the light sources

The photoreactors that have been built during this research have their own features and properties, particularly in the light sources. Each of these reactors were built to evaluate the degradation for Rhodamine B and to contribute in the main features to build the Raspberry Pi photoreactor. As observed in the experimental section all the characteristics of the light sources of the reactors were exposed in terms of dimensions, wattage, price, temperature (color), lifespan, and light intensity, Supporting Information*. All the reactors and their light sources were discussed in term of their physical properties, nevertheless the principal goal is to compare them in terms of their photo degradation activity with the Rhodamine B. Also, the understanding of the functionality of these elements provided the best features for the construction of the Raspberry Pi photoreactor, where different high power LEDS were added to have a better range in the visible light spectra. The Kessil Tuna Blue and Kessil Tuna Sun lights were used for reference in this research as these light sources are commonly used by organic chemists in photoreaction processes, also due to the ease in the functionality as one can change the intensity and color of light. The COB reactor was also analyzed, the main characteristics which they differ is in the price and the wattage, where the Cree COB ($30) is more expensive than the Chanzon COB ($10.75), also in terms of energy consumption, the Cree (129.6W) have a higher wattage than the Chanzon (96W). These differences are due to the quality of the COBs, also in their lifetime, Cree (75000-100000h) and the Chanzon (50000h). The LED reactors were analyzed within their main characteristics, the light sources of these photoreactors were high power Cree LEDs, where the number of LEDs, the structure and the distance to the sample were different for each case. For the first case, 12 Cree LEDs were used in different colors and for the second case 6 Royal Blue Cree LEDs were used, also a 44 LEDs reactor was used to compare the analysis for the photodegradation. As expected these reactors are different in terms of energy consumption and price, because of the amount of LEDs used.

Table 3: Comparison of the features included on each photoreactor/light source.

	Raspberry Pi Photoreactor	Pennoc OC Photoreactor	Kessil Tuna Blue
Fully customizable modular design	×	×	
Full control of light intensity	×	×	×
Full control of spectral wavelength	×		×
Magnetic stirring with speed control	×	×	
Active cooling	×	×	×
pH monitoring	×		
Temperature monitoring	×	×	
Autosampling	×		
Touch Screen control	×	×	

As observed in Table 3, the main features of the reference photoreactor, the reference light source and the Raspberry Pi photoreactor are presented in terms of their functionalities, where it is shown that the Raspberry Pi photoreactor includes more features. In terms of prices, the Kessil Tuna Blue costs $350, the Pennoc OC M2 $7100 and the Raspberry Pi $734.25. For the list of the total cost of the elements included in the Raspberry Pi photoreactor see *Supporting Information

Photocatalytic Activity

The photocatalytic activity of each photoreactor is evaluated by the guidelines that had been set in the experimental section. Moreover, it is shown that over time the absorbance of the RhB solution undergoes a decrease with all cases. The photocatalytic degradation of Rhodamine B can be observed for each reactor and light source. It is necessary that an experiment with a target and a control is carried out, in this case to observe that the influence of the light with the catalyst are responsible for the degradation of the dye.

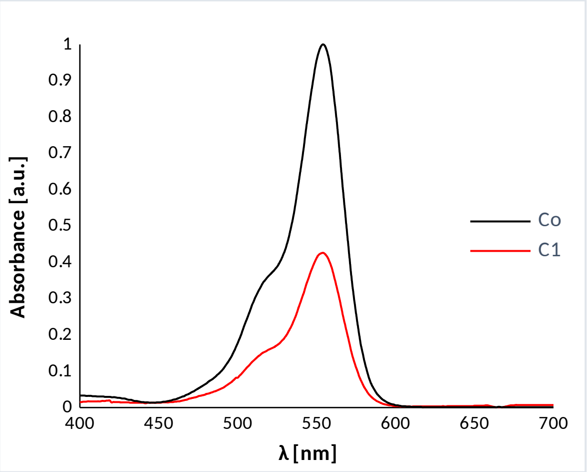


Figure 17. UV-VIS absorption spectrum of the KESSIL TUNA BLUE.

As observed in the Fig. 17 the KESSIL SUN reactor had a photodegradation of 39.2%, and the KESSIL BLUE had the highest degradation with a value of 55.9%. These values of photo degradation are the highest of all the photo reactors used in the research.

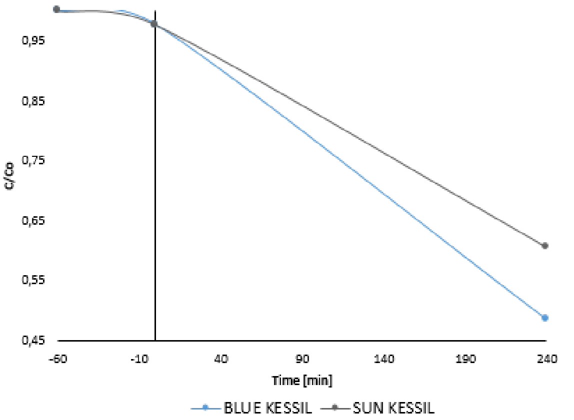


Figure 18. Photocatalytic degradation of Rhodamine B as a function of irradiation time.

Table 4: Total degradation percentage of each light source.

Light Source	Total degradation (%)
KESSIL BLUE	55.9
KESSIL SUN	39.2

The Chanzon 10000K had a photodegradation of 16.5%, the Chanzon 4000K a value of 20.8%, the Chanzon 6000K a value of 21.8%, and the Cree 5000K had the highest value for the photodegradation of RhB 35.7% of all COBs tested.

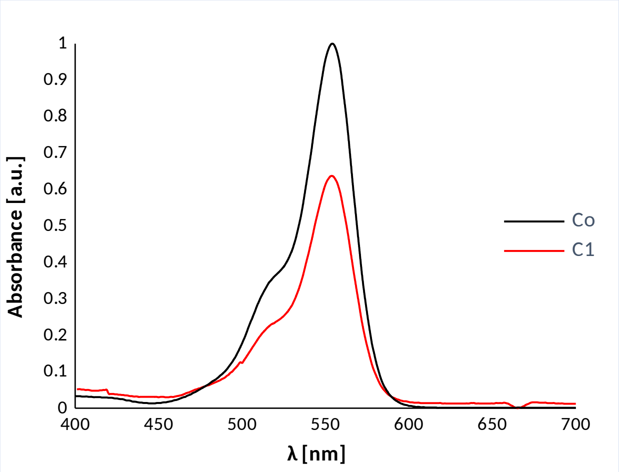


Figure 19. UV-VIS absorption spectrum of CREE 5000K COB.

Table 5: Total degradation percentage of each light source.

Light Source	Total degradation (%)
CHANZON 10000K	16.5
CHANZON 4000K	20.8
CHANZON 6000K	21.8
CREE 5000K	37.5

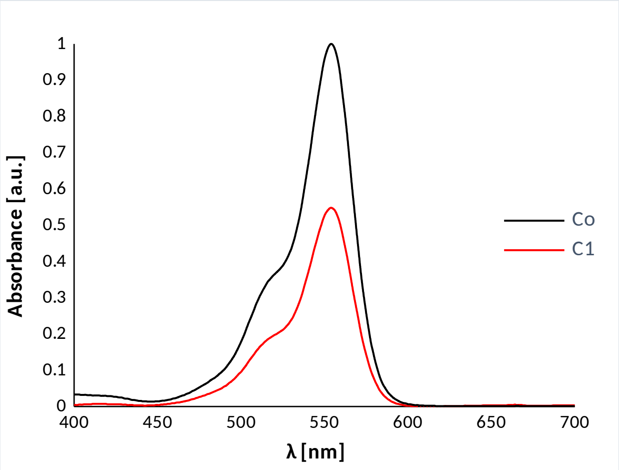


Figure 20. UV-VIS absorption spectrum of 6 BLUE LED Reactor

The 12 LEDS reactor had a photodegradation of 35.5%, the 44 LEDS reactor a photodegradation of 29%, and as observed in Fig.20 the 6 BLUE LEDS reactor had the highest 47.3%.

Table 6: Total degradation percentage of each light source..

Light Source	Total degradation (%)
12 LEDS	35.5
44 LEDS	29
6 BLUE LEDS	47.3

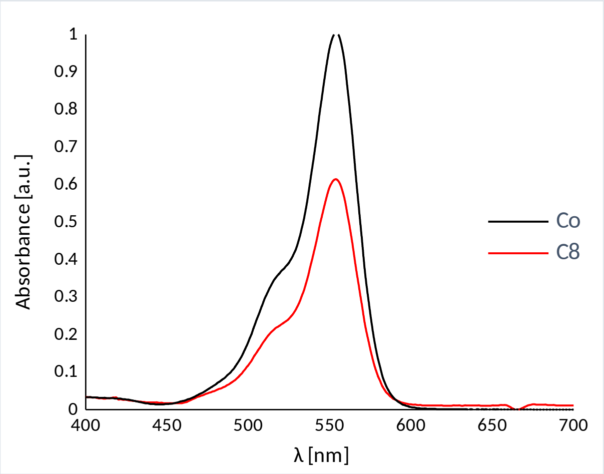


Figure 21. UV-VIS absorption spectrum of Raspberry Pi photoreactor

The Raspberry Pi photoreactor is also used in the photocatalytic reaction for the degradation of Rhodamine B, all the LEDS 100% intensity was performed by the photoreactor in this reaction. As shown in Fig. 21 the reactor had a total degradation of 39.4%.

Influence of color and light intensity on Photocatalysis

According to Table 5, it is clear that the KESSIL BLUE light source has the highest degradation with a value of 55.9% of the Rhodamine B, also the BLUE LED reactor showed a degradation of 47.3% of the dye and the Raspberry Pi reactor a value of 39.4%. According to this results, the light sources that have their spectra closest to the range of visible light in the blue color obtain higher degradation values as well as their speed in experimental time. In addition, it is observed that the number of LEDs used in the 12 LED Reactor and the 44 LEDS reactor does not show a major influence in the photodegradation of the contaminant, as observed the 6 BLUE LEDs reactor has a higher value of the degradation of the dye comparing it to the rates of the 12 LEDs reactor (35.5%) and the 44 LEDs reactor (29%). A higher amount of LEDS within the reactor require more energy consumption. The reactors that consume more energy have shown lower values. The results obtained in the photocatalysis reactions performed by (Khademalrasool, et al, 2016) research show that using 6 UV-HP LEDS 6W degrades more Rhodamine B dye (75%) than using 4 UV mercury tubes 32W (35%) in the same amount of time. As observed in the results of the total degradation of the COBs, they show lower degradation compared to the LEDs, also the Chanzon light sources show significant lower values comparing to the Cree light source, the 5000K Cree light source has shown the higher degradation rate of all COBs, with a value that is very close to the 12 LEDs reactor. As a consequence, the light source that were used to the final Raspberry Pi reactor were the Cree LEDs reducing the amount of LEDS used for photocatalytic reactions.

The results of the photodegradaion have shown that the source of blue/UV light (KESSIL) is the most efficient in terms of removal of RhB. According to the spectra of the KESSIL light, it has a presence in the UV region that helps with the degradation of the dye. For the light intensity measurements, it is observed that the Chanzon 10000K has a higher illuminance with 10900 lx, and the Cree 5000K has the lower illuminance with 8436 lx, this results show that the instruments light intensity did not show a major influence in the total degradation of the dye, as the value of the CH10000K is the lowest for the COB photoreator. In the LED reactors the 44 LED reactor show a value of 10346 lx, also the 6 Blue LED reactor a value of 8279 lx and the 12 LED reactor with the lowest value of 7875 lx, here as noticed, the light intensity does not show a significant influence on the degradation of the dye since the 44 LED reactor value of the degradation is the lowest of this group. Similar results corresponding to the influence of light intensity are reported with a continuos photoreactor (Rasoulifard, 2013) where UV LEDS were used in full intensity in the degradation of Red DR23 with $S_2O_8^{2-¿¿}$ as a semiconductor catalyst.

The main reason for this observation is the interactions among the hydroxyl radicals saturate due to the amount of photons that excite the catalyst, producing agents that does not allow oxidation reactions.

Subsequently the BiFeO3 has properties that make it more resistant to temperatures and a range in the very broad visible spectrum for its activation (Gao, et al., 2014), it has been observed that near 450 nm, that is, under the application of blue/UV light, there is greater degradation. As expected this light sources are the ones with more presence in our RPi Photoreactor, that with 20 LEDs within the visible light spectrum a high degradation was also obtained.

Influence of temperature on photocatalysis

After the analysis of the temperature behavior of the reactors, it was decided that the implementation of three fans is necessary for the cooling system of the COB photoreactor, where it is observed in Fig. 14 that the temperature has more stable values close to 29 ℃, where the placement of this system improved the temperature behavior of the other COBs. Nevertheless, with the addition of the fans the 5000K Cree COB and the 4000K Chanzon have shown a maximum temperature of 30℃ and 30.7°C, however, it is not observed that this temperature change has a significant influence of the photo degradation of the dye. These light sources show the lowest degradation values even with the addition of the fans. In the case of the LED reactors, the temperature behavior is observed, and is variable for the two reactors, where it is observed that the 44 LED reactor has values up to 32 ℃, and the CREE LED 12 reactor has values close to 31 ℃.

It is shown that the KESSIL BLUE light source has reached a temperature of 33 ℃, also the Raspberry Pi photoreactor has the highest temperature value with 45° C, however, it is observed that these reactors have the highest values of photocatalytic degradation. Although the temperature reaches high values, other researchers have not found a considerable dependence. It is observed that there is a correct activation of the catalyst surface Bismuth Ferric (BiFeO3) due to the work of the light spectrum where the reaction is subjected even when the reaction reaches a value of 80° C (Muradov et al., 1996; Fu et al., 1996; Chen and Ray, 1998; Rincon Pulgarin, 2003; Evgenidou et al., 2005) . The same results are obtained in other photocatalytic processes (Rasoulifard, 2013) where the degradation of an organic dye is achieved in temperatures close to the 55 ℃, also in photocatalytic reactions performed by commercially available reactor is reported that within 25 - 60 ℃ the degradation of dyes are not affected in a major way (Chi Le, 2017).

The results of the temperature analysis have shown that there is not a significant temperature dependence in the values of the photodegradation, nevertheless this research provides results only for a standard catalyst which may change in further investigations, in consequence, the Raspberry Pi photoreactor has one fan that allows cooling and agitation of the sample, however, in future works will be needed to construct a lid that also will have fans to ensure the stabilization of temperature in this reactor.

Conclusions

In this research, the photo degradation of Rhodamine B using various light sources and reactors with different structures has been explored in order to find the best conditions for the construction of the Raspberry Pi controlled Photoreactor.. Different COBs, high power LEDs, and a reference light source have been used to explore the right conditions that a photo catalysis process must have, these conditions helped to understand the characteristics and features that must be included in the Raspberry Pi Photo reactor. It is demonstrated, that the construction of a low cost high quality Raspberry Pi controlled photoreactor is possible in developing countries where the technology variety is limited and sometimes difficult to obtain. The construction of this reactor allows the control of all the features needed to have a successful photo catalysis, this device can control the color/intensity of the lights embedded, also the monitoring of the pH and temperature of the sample, and also a autosampling system has been added to obtain a certain volume of the sample in the time that is needed. In the evaluation of the photo degradation of the Rhodamine B the results have shown that certain light sources degraded the contaminant with different degradation percentages. In this case, as expected the reference KESSIL BLUE light had the best results with a degradation of 55.9%, this reactor also reached a temperature with a value of 33℃, in addition, the Raspberry Pi photoreactor obtained one of the highest degradation values with 39,7% and the highest value of the temperature 45℃ indicating that the temperature does not interfere in a major way in the results. The lights that were added to the final reactor were Royal Blue and also a broad range in the UV area for optimizing the degradation conditions.

Furthermore, the number of high power LEDs did not show a major influence on the photo degradation of the organic dye Rhodamine B, as observed comparing the 12 LEDS reactor with the 44 LEDS reactor it is showed that the first one degraded 6% more than the other, also the 6 BLUE LED reactor showed a higher degradation than the 12 LED reactor with 11.8% more degradation of the dye. These results clearly reveal that a successful photo degradation does not depend on the quantity of the high power LEDs, whereas this dependence might lay on the spectrum and intensity of the light sources. In addition, the research outcomes showed that photocatalytic processes using a variety of light sources could degrade the Rhodamine B concentration over time, where the light source must be the source of energy that helps to activate the catalyst, it is necessary that further investigations with other catalysts materials must be done particularly with materials that can activate using all the visible light spectra. The photocatalysis using standard BFO and the Raspberry Pi Photoreactor for photocatalytic oxidation processes is recommended to be a promising mechanism for the degradation of dyes from textile wastewater.

Associated Content

*Supporting Information. The supporting information document is available where the graphics, procedures and diagrams are detailed.

Acknowledgements

Thanks to Thomas Cadenbach for his patience and extensive knowledge that prompted me to develop this work. To the professors and assistants of the Environmental Engineering department, to the *EMA-USFQ* Atmospheric Measurement Station for the use of their equipment and facilities. To my parents, to my brother and especially to my sister Pamela who inspired me to continue this career and gave me the strength to complete this work.

References

Avila, A. Bahamonde, J. Blanco, B. Sánchez, A.I. Cardona y M. Romero, Applied Catalysis B. Environmental, 17, 75-88 (1998).

Barr, Michael. 2001. "Introduction to Pulse Width Modulation (PWM)". Barr Group.

Bhatkhnade, D.S., Kamble, S.P., Sawant, S.B., Pangarkar, V.G., 2004. Photocatalytic and photochemical degradation of nitrobenzene using artificial ultraviolet light.

Chen, D., Ray, A.K., 1998. Photodegradation kinetics of 4- nitrophenol in TiO2 suspension. Water Res.

Chi Le, Michael K. Wismer, Zhi-Cai Shi, Rui Zhang, Donald V. Conway, Guoqing Li, Petr Vachal, Ian W. Davies, and David W. C. MacMillan. A General Small-Scale Reactor to Enable Standardization and Acceleration of Photocatalytic Reaction. †Merck Center for Catalysis at Princeton University, Princeton, New Jersey, United States (2017)

Chin, S.S., Chiang, K., Fane, A.G., 2006. The stability of polymeric membranes in TiO2 photocatalysis process.

Evgenidou, E., Fytianos, K., Poulios, I., 2005. Semiconductorsensitized photodegradation of dichlorvos in water using TiO2 and ZnO as catalysts

Deblonde, T., Cossu-Leguille, C. and Hartemann, P., Emerging pollutants in wastewater: A review of the literature. International Journal of Hygiene and Environmental Health. 2011

Gaya, U.I., Abdullah, A.H., 2008. Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems. J. Photochem. Photobiol. C: Photochem.

Harris, D. Quantitative Chemical Analysis. Michelson Laborator. Eight Edition. W.H Freeman and Company- 2010

Katic, Pamela L. dos Santos, Joyce G. Gabriel, Acacia Adriana Salomão and Juliano Alves Bonacin. ASSEMBLY OF LOW-COST LAB-MADE PHOTOREACTOR FOR PREPARATION OF NANOMATERIALS. Instituto de Química, Universidade Estadual de Campinas, 13083-970 Campinas – SP, Brasil. 2017

Jhonson. High-Power, Short-wave LED purifies Air 2003.

Khademalrasoola M, Farbodb M, Talebzadeh M-D. Theimprovement of photocatalytic processes: Design of a photoreactor using high-power LEDs. Department of Basic Sciences, Jundi-Shapur University of Technology, Dezful, Iran. 2016.

Lighting Industry Federation. 1994. Lighting Industry Federation Lamp Guide. London: Lighting Industry Federation.

Ministerio de Industrias y Productividad. 2016. La industria textil es el segundo sector que genera más empleo en el país. Recuperado el 10 de abril del 2019 https://www.industrias.gob.ec/

Miron, Rich. 2016. The basics of Chip on Board LEDS. https://www.digikey.com/en/articles/techzone/2016/aug/the-basics-of-chip-on-board-cob-leds

Muradov, N.Z., Raissi, A.T., Muzzey, D., Painter, C.R., Kemme, M.R., 1996. Selective photocatalytic degradation of airborne VOCs.

Nguyen, J.; Matsuura, B.; Stephenson, C. J. Am. Chem. Soc. 2014, 136, 1218

O. Legrini, E. Oliveros, A.M. Braun, Chem. Rev. 93 (1993) 671.

Ochuma, I.J., Fishwick, R.P., Wood, J., Winterbottom, J.M., 2007. Optimisation of degradation conditions of 1,8-diazabicyclo[5. 4.0]undec-7-ene in water and reaction kinetics analysis using a cocurrent downflow contactor photocatalytic reactor.

Ortiz-Quiñonez J, Díaz D, Zumeta-Dube H, Arriola-Santamaría I, Betancourt P,Jacinto S, Nava-Etzan N. Easy Synthesis of High-Purity BiFeO3Nanoparticles: New InsightsDerived from the Structural, Optical, and Magnetic Characterization. Departamento de Química Inorganica y Nuclear,04510, Mexico City, Mexico, 2013.

Papadas, I., Kota, S., Kanatzidis, M. y Armatas, G. (2012). Templated Assembly of BiFeO3 Nanocrystals into 3D Mesoporous Networks for Catalytic Applications. The Royal Society of Chemistry. DOI: 10.1039/ x0xx00000x

Rincón, A.G., Pulgarin, C., 2003. Photocatalytical inactivation of E. coli: effect of (continuous-intermittent) light intensity and of (suspended-fixed) TiO2 concentration.

Schneider, J., Matsuoka, M., Takeuchi, M., Zhang, J., Horiuchi, Y., Anpo, M., & Bahnemann, D. (2014). Understanding TiO2 Photocatalysis: Mechanisms and Materials. American Chemical Society, 114, 9919-9986. doi:10.1021/cr5001892

Teng Chang Jiu, Dan Xie, Meng-xing Sun, Jian-long Xu, Chun-song Zhao, Pu Yang, Yi-lin Sun, Cheng Zhang, Xian Lia. (2013) Sucrose-templated nanoporous BiFeO3 for promising magnetic recoverable multifunctional environment purifying applications: adsorption and photocatalysis. Tsinghua University, Beijng, China.

Torres-Luna JA, Carriazo JG y Sanabria NR. 2016. Delaminated montmorillonite with iron(III)-TiO2 species as a photocatalyst for removal of a textile azo-dye from aqueous solution. Environmental Technology, 37: 1346-1356.

Urkiaga A., Gómez L., Gutiérrez M. 2011, Aplicación de procesos de oxidación avanzada al tratamiento de efluentes de diferentes sectores industriales. http://cidta.usal.es/residuales/libros/logo/pdf/oxidacion_avanzada_efluentes_industriale s.pdf

Volatier, D. Duchesne, R. Morandotti, R. Ares, V. Aimez, Extremely high spect ratio GaAs and GaAs/AlGaAs nanowaveguides fabricated using chlorine ICP etching with N2-promoted passivation, Nanotechnol 21 (2010).

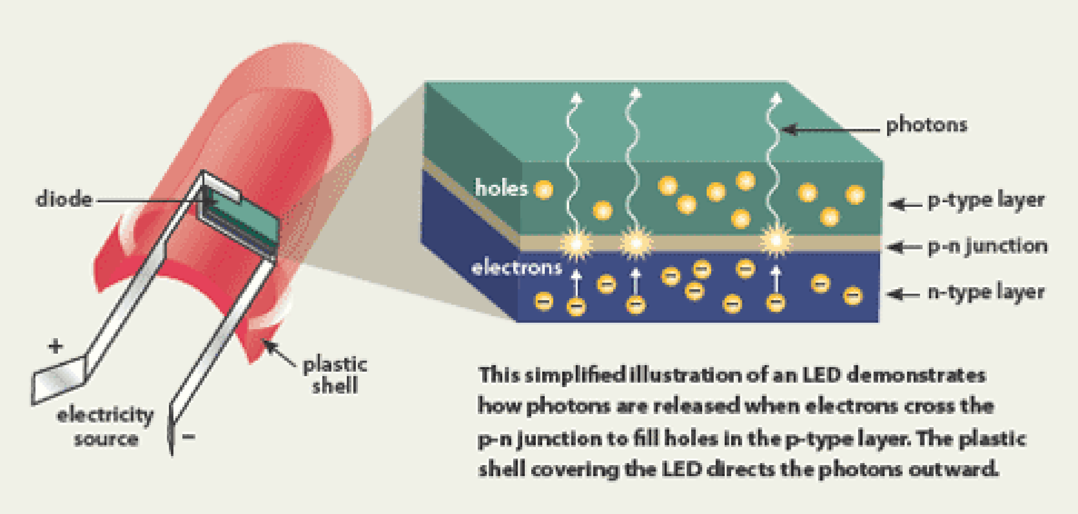
Walsh, JWT. N.d. Textbook of Illuminating Engineering. Londres: Pitman.

Xiaohui Deng, Kun Chen and Harun Tüysüz*, A Protocol for the Nanocasting Method: Preparation of Ordered Mesoporous Metal Oxides. Max-Planck InstitutfürKohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Ge

SUPPORTING INFORMATION

Light Emitting Diodes

The operation of the LEDs is based on a principle called electroluminescence. An LED is a special type of diode that is designed to give off light, this diode is forward-biased so the electrons and holes are moving back and forth in the junction of n-ytpe and p-type silicon semiconductors. After an electron moves from the n-p junction it will combine with a hole and disappear, this process will make an atom complete and more stable giving off a little burst of energy in the form of a photon of light, as showed in Fig. 2. The color of the light is emitted according to the semiconductor energy band.



This simplified illustration of an LED demonstrates how photons are released when electrons cross the p-n junction to fill holes in the p-type layer. The plastic shell covering the LED directs the photons outward.

Figure 1. LED configuration and functioning

Figure 2. Structure of the LED light sources that will be used for the construction of the reactors

In this research work, Chip on board (COBs) LEDs were used, which work based on series connections of multiple very small LEDs which are placed directly on a ceramic/ aluminum substrate usually in a single module. Thanks to the reduction of components and the elimination of the traditional packing structure they have a better performance in heat dissipation, particularly when paired with an external heat sink (Miron, 2016).

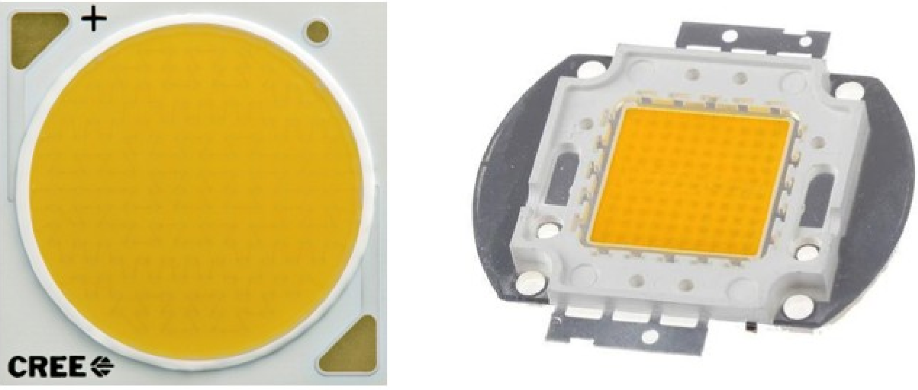


Figure 3. Structure of the COB LED light sources that will be used for the construction of the reactors

REFERENCE LIGHT SOURCE

Table 1: Reference light source characteristics

Light Source	**Dimensions (mm)**	**Voltage (V)**	**Current (mA)**	**Wattage (W)**	**Price ($)**	**Temperature (K)**	**Lifespan (h)**
KESSIL TUNA BLUE	63.5 Diámetro	19-24	4740	90	350	10000-12000	>100000
KESSIL TUNA SUN	63.5 Diámetro	19-24	4740	90	350	6000-9000	>100000

Temperature Behavior

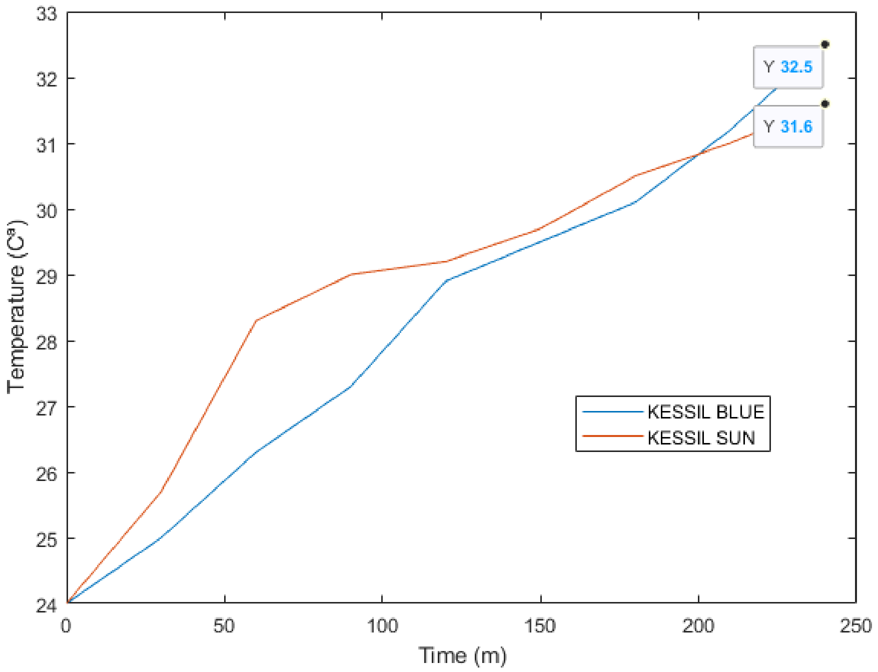


Figure 4. Temperature Behavior of the references light sources.

Light intensity measurements

Light intensity is defined in two concepts, luminance and illuminance. Luminance is a form of light energy which is perceived by the human eye, which is, the brightness of the light that is emitted and then reflected by an object. On the other hand, the illuminance is the measurement of the amount of light that manages to expand in a medium (surface), the unit to measure the luminance is the Lux (lx).

Table 2: Light intensity values of light source

Light Source	**Lumen/m2**
KESSIL TUNA BLUE 100%	8457
KESSIL WHITE 100%	9346
KESSIL BLUE 50% WHITE 50%	9502

LED Photoreactors

Table 3: Light sources used in the LED Photoreactors.

Light Source	Dimensions (mm)	Voltage (V)	Current (mA)	Wattage (W)	Price ($)	Temperature (K)	Lifespan (h)
12 CREE LEDs	20 Diámetro	2.85 (x12)	3000	8.55 (X12)	4.25 (X12)	5000-8300	75000-100000
6 ROYAL BLUE LEDS	20 Diámetro	3.45 (x6)	3000	10.35 (X6)	5 (x6)	12500	75000-100000

12 CREE LEDS Photoreactor

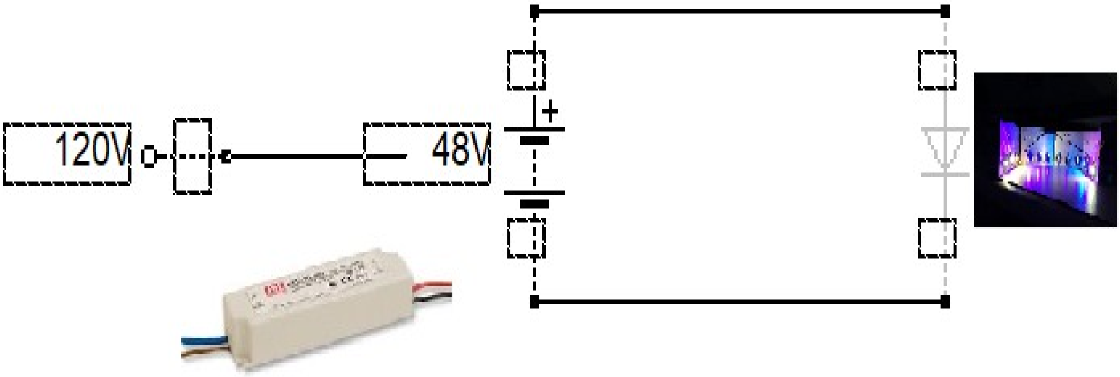


Figure 5. Configuration of the 12 Cree LEDs Photo Reactor

6 ROYAL BLUE LEDS Photoreactor

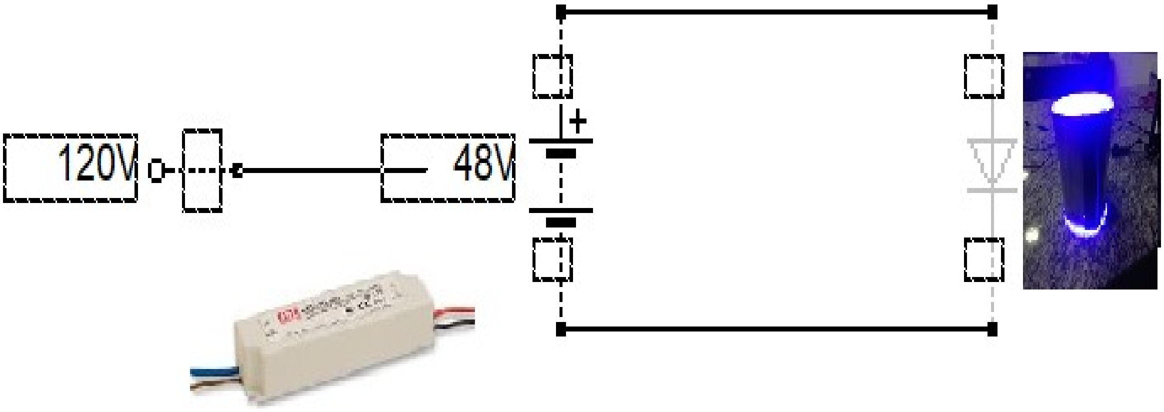


Figure 6. Configuration of the Royal blue LEDs Photoreactor

Temperature Behavior

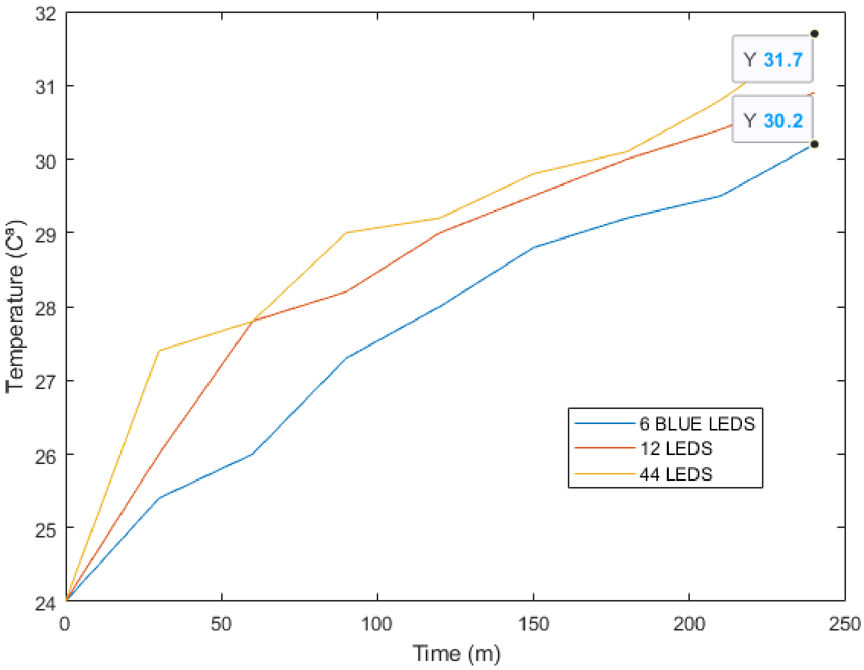


Figure 7. Temperature behavior of LED reactors

Light intensity measurements

Table 4: Light intensity values of each instrument

Light Source	Lumen/m^2
44 LED REACTOR	10346
12 LED REACTOR	7875
6 BLUE LED REACTOR	8279

2.1.1 COB Photoreactor

Table 5: Light sources used in the COB Photoreactor.

Light Source	Dimensions (mm)	Voltage (V)	Current (mA)	Wattage (W)	Price ($)	Temperature (K)	Lifespan (h)
CREE COB LED	34.85 x 34.85 x 1.7	36	3600	129.6	30	6500	75000-100000
CHANZON COB LED	127 x 101.5 x 0.5	30-32	3000	96	10.05	4000-4500	50000
CHANZON COB LED	127 x 101.5 x 0.5	30-32	3000	96	10.05	6000-6500	50000
CHANZON COB LED	127 x 101.5 x 0.5	30-32	3000	96	10.05	10000-10500	50000

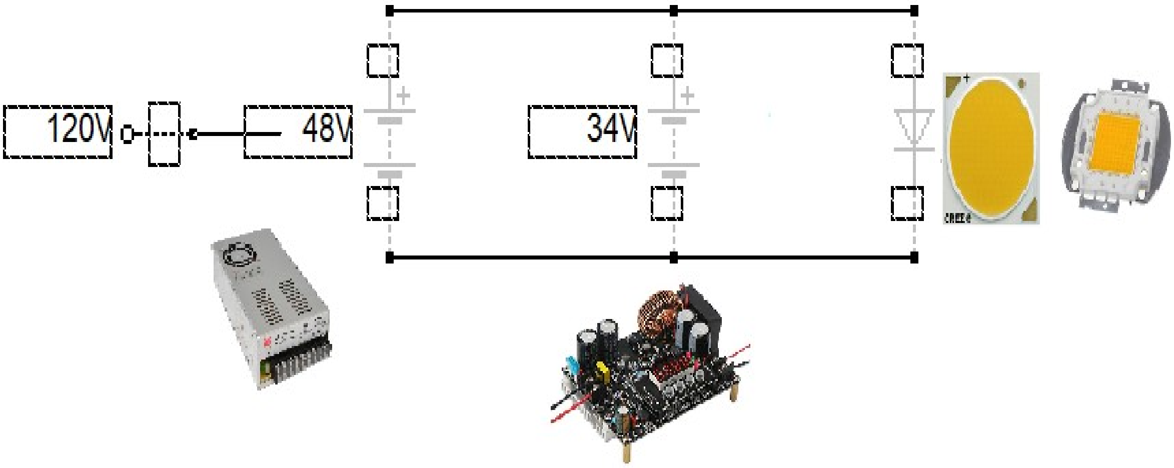


Figure 8. Configuration of the COB Photoreactor

Cooling system

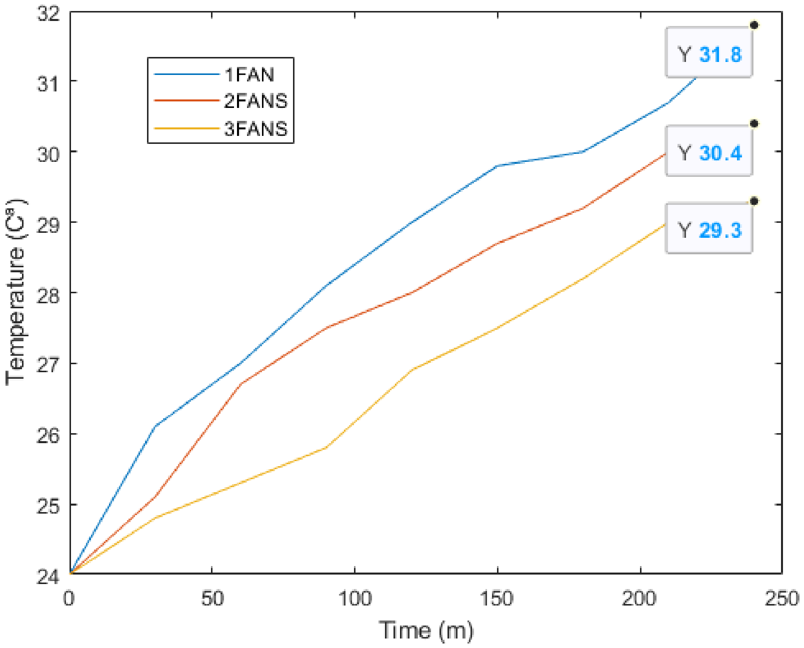


Figure 9. Temperature behavior with the addition of fans in the system

Light intensity measurements

Table 6: Light intensity values of light source

Light Source	Lumen/m$_2$
CHANZON 10000K	10900
CHANZON 6000K	9804
CHANZON 4000K	8645
CREE 6500K	8436

RASPBERRY PI Photoreactor

REEF PI

Electronic Materials. –

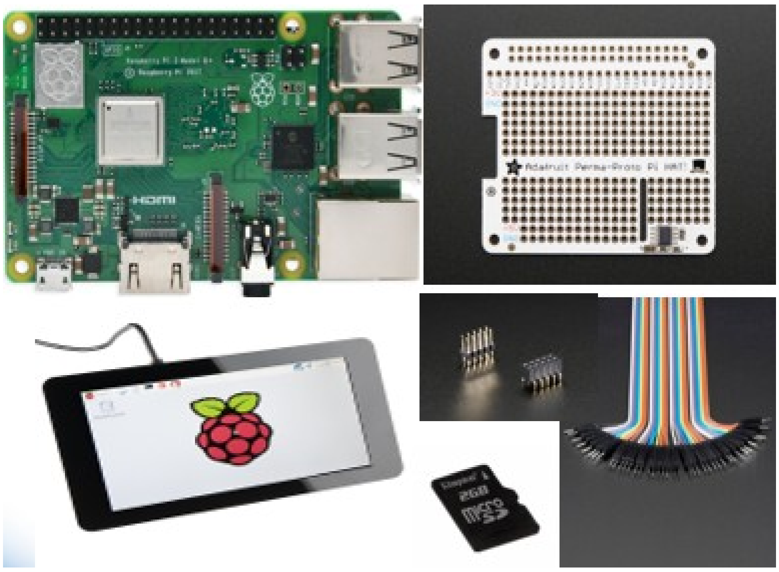


Figure 10. Raspberry Pi 3 Model B +, Perma-Proto Board Pi HAT Adafruit, Female and male jumper cables, Female and male pins, Rasperry Pi. Touch Screen LCD 7’’, SD Card 32 Gigabytes. [Source: https://learn.adafruit.com/users/ranjib](https://learn.adafruit.com/users/ranjib)

Configuration of the Raspbian Operating System and Reef Pi 2.5 software

First of all is necessary to configure the operating system within our Raspberry Pi in order to obtain the REEF-PI open software through an internet browser, the operating system that is used is Raspbian which is recommended for this type of applications.

Here are the instructions necessary for the installation (Dey, 2017):

On your main computer with Windows, Mac or Linux:

A. Format an SD card

- Download SD card formatter

- Format an SD card with formatter

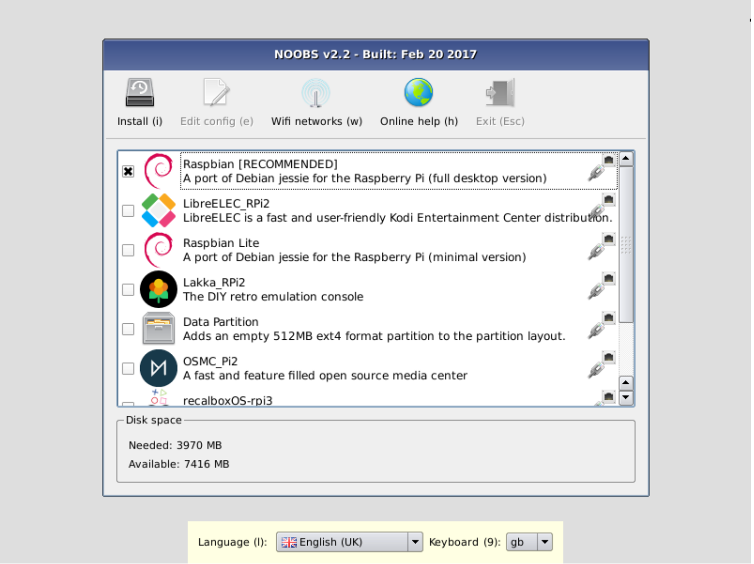
B. Download the Raspberry Pi "NOOBS" file

https://www.raspberrypi.org/downloads/noobs/

C. Extract the NOOBS file to the formatted SD card

D. Insert the SD card with "NOOBS" into Raspberry Pi

E. Turn on the screen and pi. Select the operating system "Raspbian" and click "install"



☒ Raspbian [RECOMMENDED]
A port of Debian jessie for the Raspberry Pi (full desktop version)

☐ LibreELEC_RPi2
LibreELEC is a fast and user-friendly Kodi Entertainment Center distribution.

☐ Raspbian Lite
A port of Debian jessie for the Raspberry Pi (minimal version)

☐ Lakka_RPi2
The DIY retro emulation console

☐ Data Partition
Adds an empty 512MB ext4 format partition to the partition layout.

☐ OSMC_Pi2
A fast and feature filled open source media center

recalboxOS-rpi3

Needed: 3970 MB
Available: 7416 MB

Language (l): English (UK) Keyboard (9): gb

Figure 11. Installation of the Raspbian operating system.

Source: https://learn.adafruit.com/users/ranjib

F. Open Raspbian Wi-Fi settings and log in to your network

G. Open the Raspbian terminal and perform:

```
sudo apt-get update -y
sudo apt-get upgrade -y
```

password (now change the stock password to something custom)

H. Set time zone:

Open the Raspbian terminal and perform:

```
sudo raspi-config
```

- Select "Location options" from the list

- Select "Change time zone"
- Follow the prompts to set the appropriate time zone

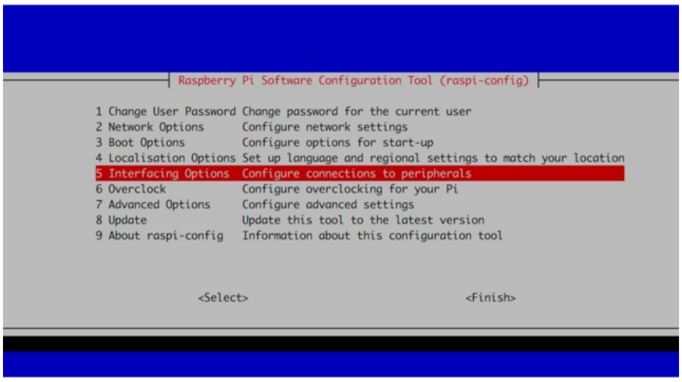
Configure Raspberry Pi modules:

I. Active SSH, SPI, I2C, UART and 1-WIRE

- Open the Raspbian terminal and perform:

sudo raspi-config

- Select "Interface Options" from the list

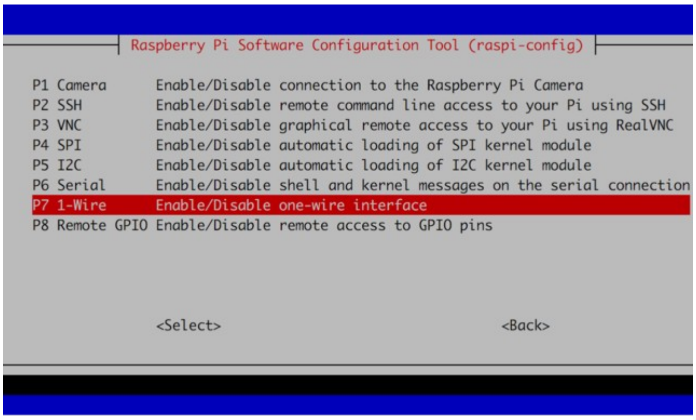


```
Raspberry Pi Software Configuration Tool (raspi-config)

1 Change User Password Change password for the current user
2 Network Options      Configure network settings
3 Boot Options         Configure options for start-up
4 Localisation Options Set up language and regional settings to match your location
5 Interfacing Options  Configure connections to peripherals
6 Overclock            Configure overclocking for your Pi
7 Advanced Options     Configure advanced settings
8 Update               Update this tool to the latest version
9 About raspi-config   Information about this configuration tool

          <Select>                    <Finish>
```

Figure 12. Interface options

Source: https://learn.adafruit.com/users/ranjib

- Select and activate SSH, SPI, I2C, Serial (uart) and 1-wire



```
Raspberry Pi Software Configuration Tool (raspi-config)

P1 Camera      Enable/Disable connection to the Raspberry Pi Camera
P2 SSH         Enable/Disable remote command line access to your Pi using SSH
P3 VNC         Enable/Disable graphical remote access to your Pi using RealVNC
P4 SPI         Enable/Disable automatic loading of SPI kernel module
P5 I2C         Enable/Disable automatic loading of I2C kernel module
P6 Serial      Enable/Disable shell and kernel messages on the serial connection
P7 1-Wire      Enable/Disable one-wire interface
P8 Remote GPIO Enable/Disable remote access to GPIO pins

          <Select>                    <Back>
```

Figure 13. Interface options

Source: https://learn.adafruit.com/users/ranjib

J. Return to the terminal and restart:

sudo reboot

Install Reef Pi 2.5

A. Open your web browser from Raspbian's desktop and navigate to https://reefpi.github.io

B. Navigate to the "General guides", "Installation and configuration" page, Scroll down to the "Install reef-pi" section and select the linked text "release"

C. This will take you to the most recent version of reef-pi, where you can extract the Pi Zero O Pi 3 .deb link depending on which Raspberry Pi you have.

D. Right-click on your version and select "copy link address"

E. Download your reef-pi software. In the terminal:

```
wget -c (and paste the copied link address starting with http ...)
```

F. Unpack the download. In the terminal:

```
sudo dpkg -i reef-pi-2.5-pi3.deb
```

- Notice how "2.5" and "pi3" stand out, 2.5 represents the version and pi3 represents that it is for the Pi 3 model. It must have the correct characters that match your download. Correct it to whatever your download version.

G. Verify that reef-pi is running using the terminal command:

```
sudo systemctl status reef-pi.service
```

- Somewhere in the text should include "active (in execution)" in light green if it is correct.

H. Find the IP address of your Raspberry Pi

- Place the cursor on the "wifi" tab on the Raspbian desktop toolbar
- It will list its "wlan0" ports. Copy the IP number that appears. They should look something like "192.168.0.2/24".
- Type the numerical address in the web browser bar of your Raspberry.
- The Reef Pi "Login" screen will open.

I. The default username and password of reef-pi are set to reef-pi.

Once the installation of the operating system and the necessary software for the control of the reactor functions is carried out, then it is necessary to build the electronic circuits inside the Perma-Proto board Pi HAT board for each of the applications.

Configuration and testing. -

LED light control. –

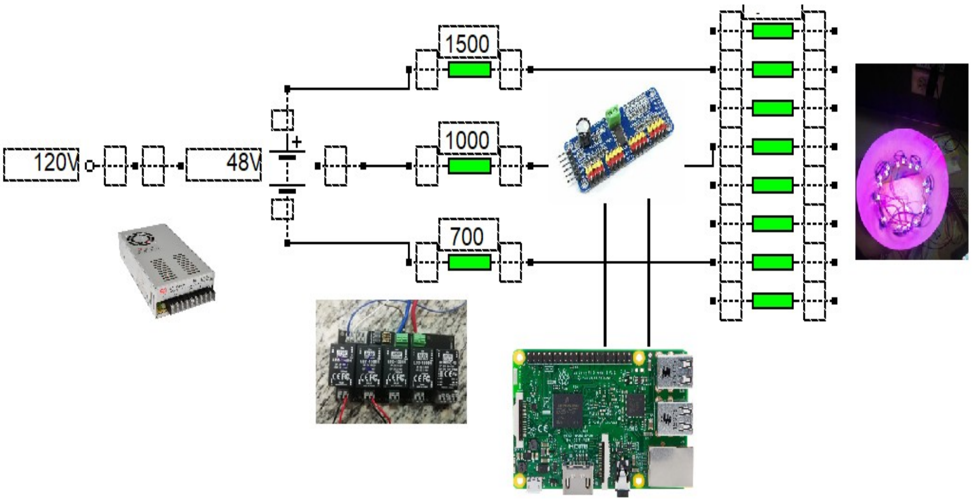
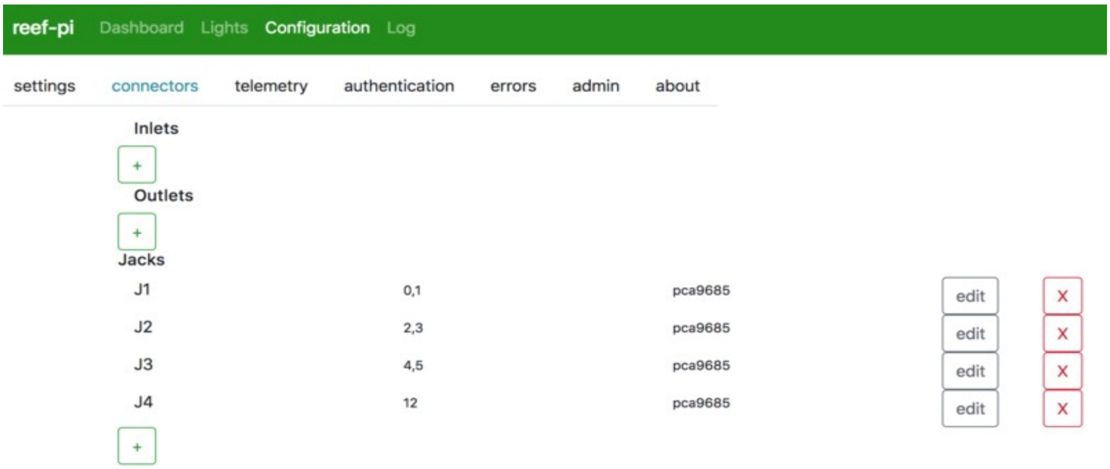


Figure 14. Light controller circuit diagram.



Jacks

J1	0,1	pca9685	edit	X
J2	2,3	pca9685	edit	X
J3	4,5	pca9685	edit	X
J4	12	pca9685	edit	X

Figure 15. Reef pi configuration

[Source: https://learn.adafruit.com/users/ranjib](https://learn.adafruit.com/users/ranjib)

For the consfiguration of the LED lights in the Reef-pi system, the PWM jacks need to be declared in the connectors tab choosing the PCA9685 as the controller for the dimming. Later, in the Lights tab every light need to be assign for each color. Here you can choose the name, color, the minimum, the maximum profile or a fixed profile fir each color of LED.

Name (pin 4)	Color	Behavior	Min	Max	Start
Intensity	🟦	Active Low	14	80	0

Profile ● Fixed ○ Auto ○ Diurnal

36

Name (pin 5)	Color	Behavior	Min	Max	Start
Spectrum	🟪	Active Low	0	100	0

Profile ● Fixed ○ Auto ○ Diurnal

35

Figure 16. Reef pi configuration

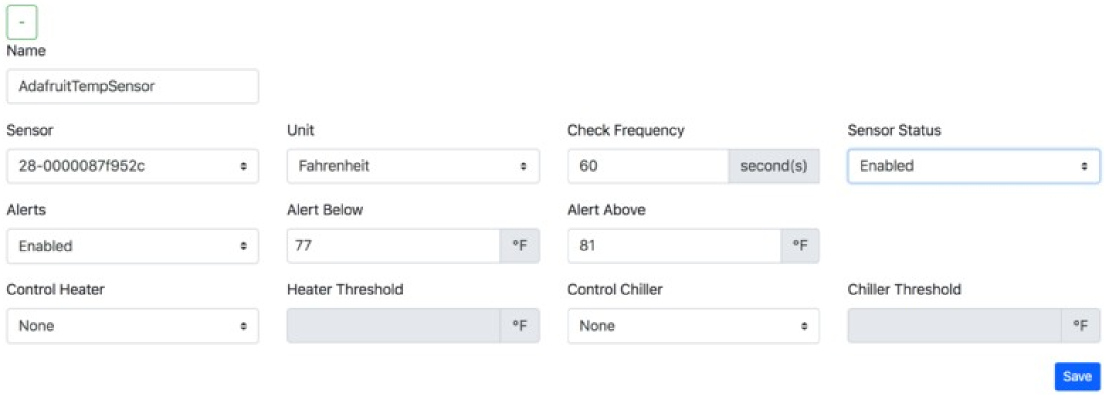
Source: https://learn.adafruit.com/users/ranjib

Temperature sensor

Figure 17. DS1820 sensor**.** Configuration of the board for temperature sensors.

Source: https://learn.adafruit.com/users/ranjib

For the configuration of the temperature sensors, the DS18B20 sensor is recognized in the Temperature tab, here the name of the sensor will appear, where units, the frequency of the data taking is selected. Also an alert of the maximum or minimum values are specified as desired.



Name

AdafruitTempSensor

Sensor	Unit	Check Frequency	Sensor Status
28-0000087f952c	Fahrenheit	60 second(s)	Enabled
Alerts	Alert Below	Alert Above	
Enabled	77 °F	81 °F	
Control Heater	Heater Threshold	Control Chiller	Chiller Threshold
None	°F	None	°F

Figure 18. Reef pi configuration

Source: https://learn.adafruit.com/users/ranjib

pH meter

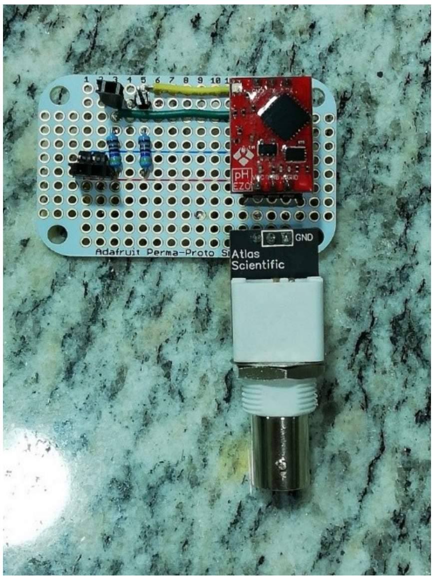
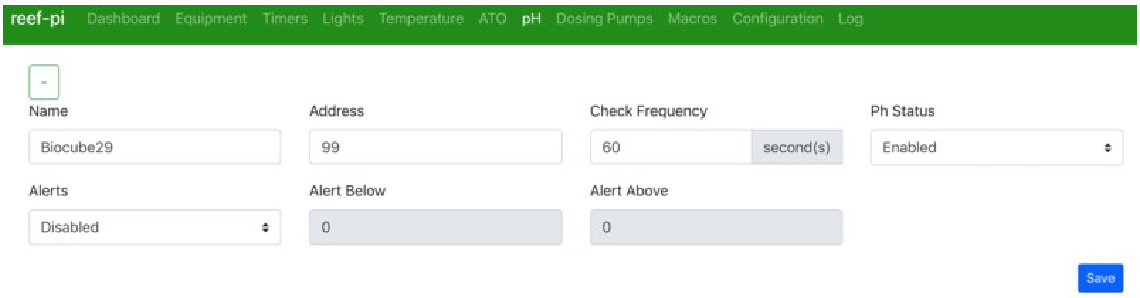


Figure 19. pH meter circuit

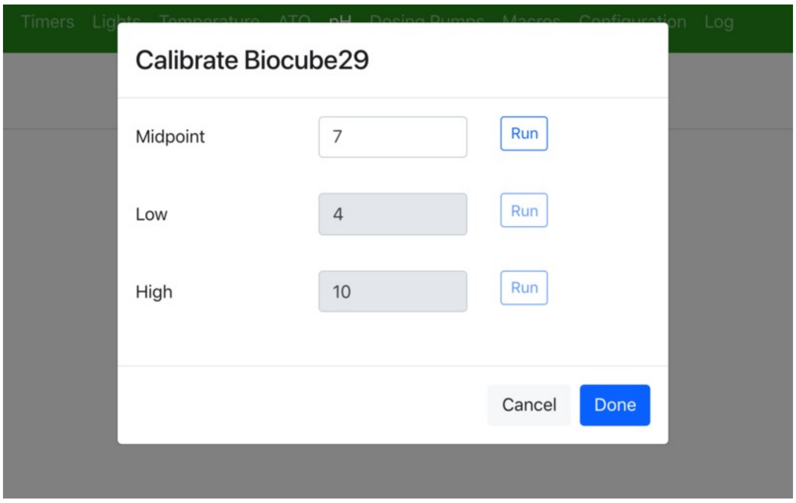
For the pH meter the probe needs to be recognized by the system, here the name of the probe is selected, also the I2C address which is 99 for default. For the calibrating of the probe the pH status has to be enabled, then the calibration solutions are read in the software, in a mid-7, low 4 and high 10 value.



Name: Biocube29
Address: 99
Check Frequency: 60 second(s)
Ph Status: Enabled
Alerts: Disabled
Alert Below: 0
Alert Above: 0

Figure 20. Reef pi configuration

Source: https://learn.adafruit.com/users/ranjib



Calibrate Biocube29

Midpoint: 7
Low: 4
High: 10

Figure 21. Reef pi configuration

Source: https://learn.adafruit.com/users/ranjib

Autosampling system

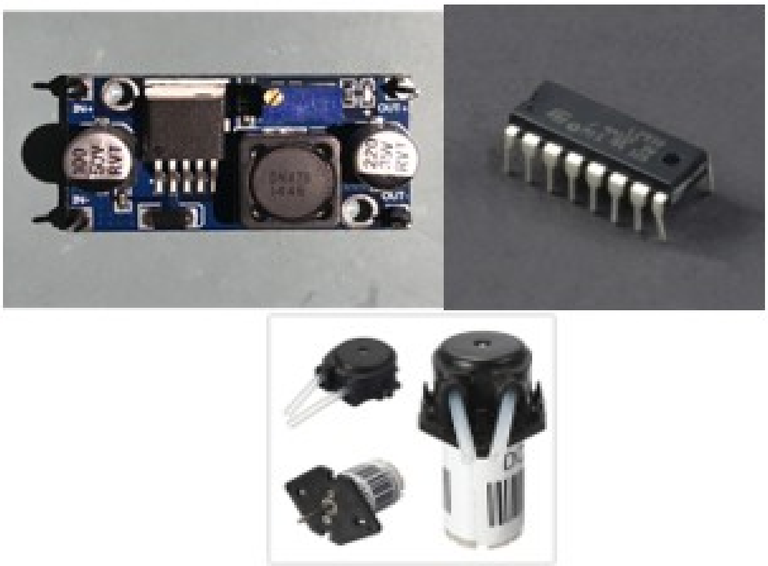


Figure 22. L293D converter, LM265 motor, Peristaltic pump

Source: https://learn.adafruit.com/users/ranjib

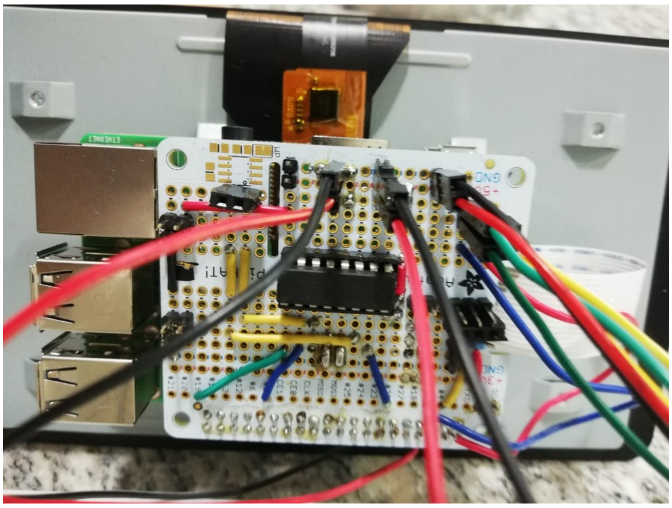
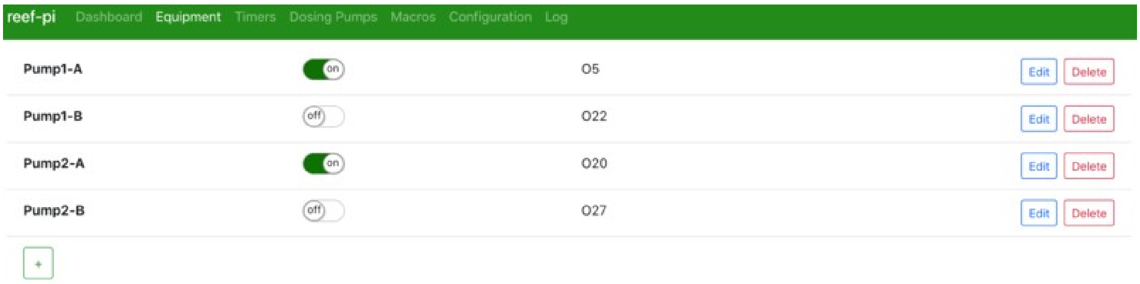


Figure 23. Autosampling circuit

For the configuration of the autosampling system also two PWM jacks need to be decalred in the connectors tab, this time RPi PWM is selected, then in the Equipment tab these jacks are added to control each direction of the pump, two jacks for each pump, where one has to be on and other one need to be off.



Pump1-A	on	O5
Pump1-B	off	O22
Pump2-A	on	O20
Pump2-B	off	O27

Figure 24. Reef Pi configuration

Source: https://learn.adafruit.com/users/ranjib

Cooling and Agitation system

The cooling and stirring system is constructed with an Arctic fan, Nd magnets and a PWM Motor Speed Controller DC Display Switch 6-30V 8A. Also we need a 12V power supply, for this the LDD drivers that has a 12V input within the same drivers are used. With this device it will be able to control the speed of the stirring system and will allow the reactor the cooling that is needed. Here the Nd magnets are placed in the fan, the fan is connected to the velocity controller, this velocity controller is connected to the 12V input in the LDD Drivers of the lights and the On/Off switch

Figure 25. PWM Motor Speed Controller DC Display, Arctic fan

3D design and Assembly

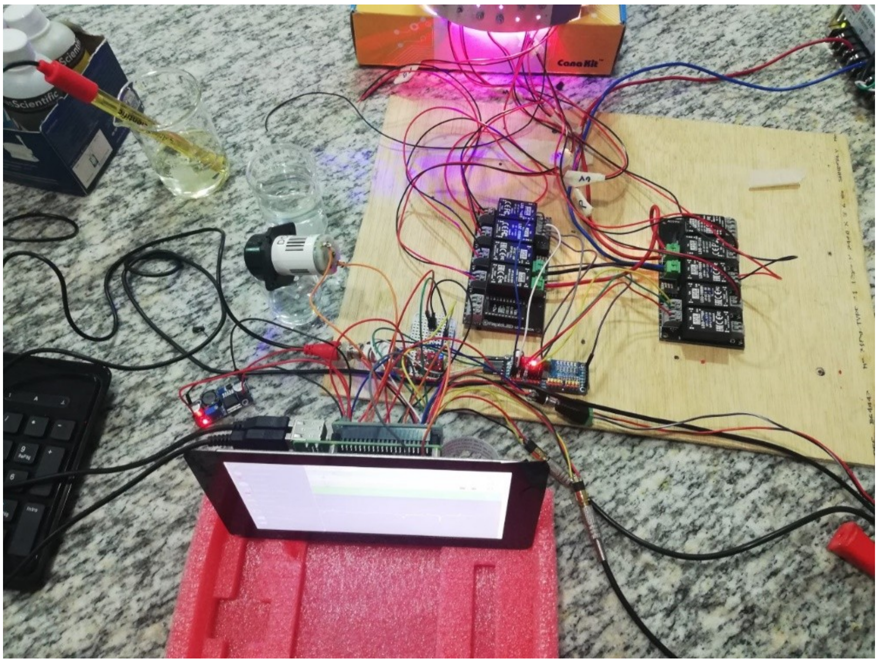


Figure 26. Electronics of all the features in the reactor

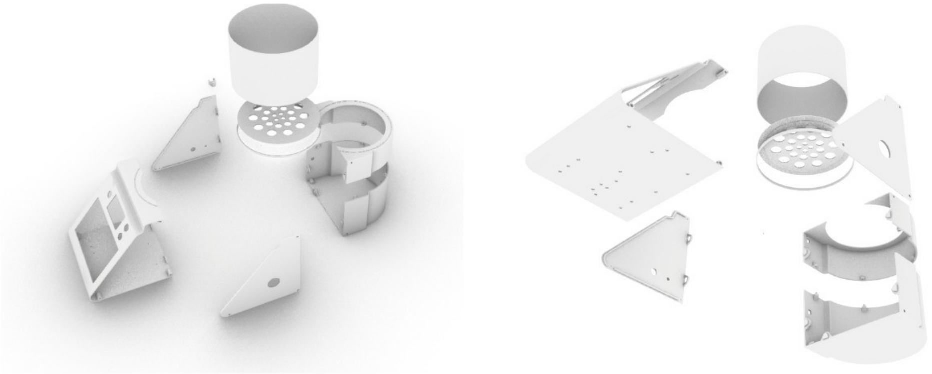


Figure 27. 3D design of the Photo Reactor

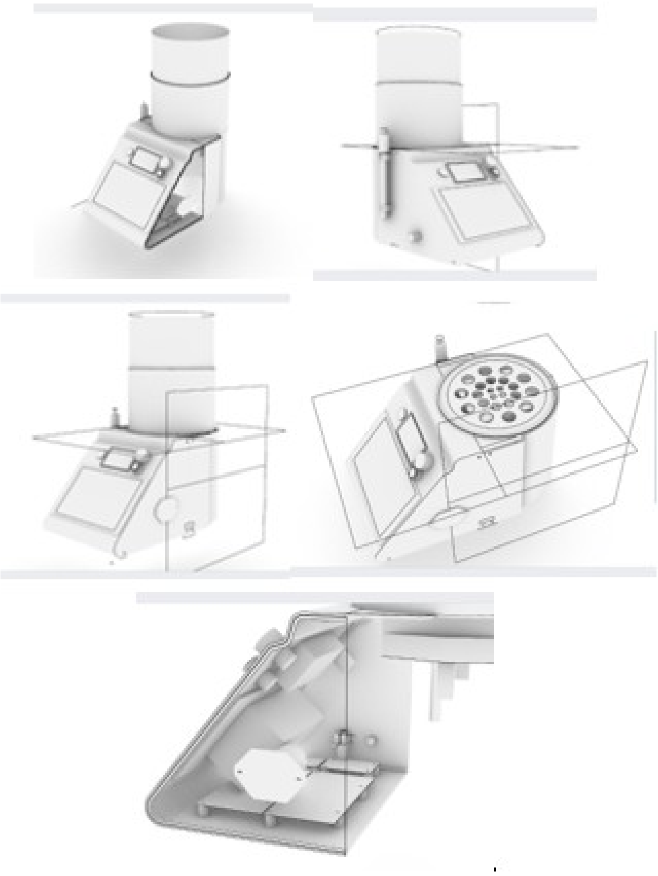


Figure 28. 3D design of the Photo Reactor

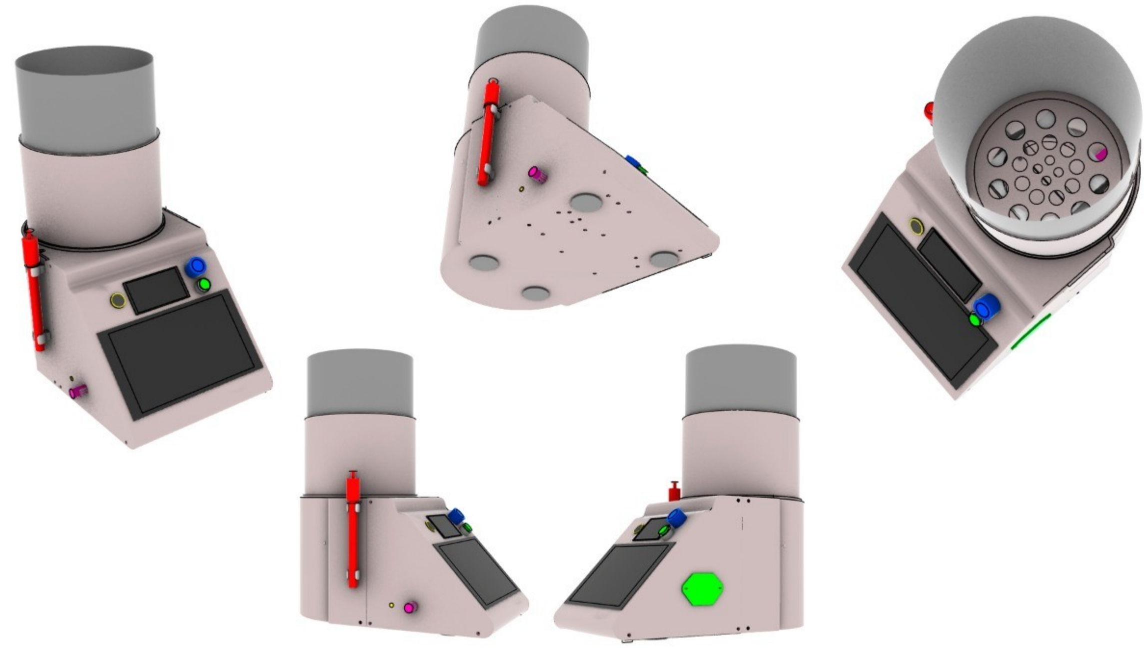


Figure 29. 3D design of the Photo Reactor

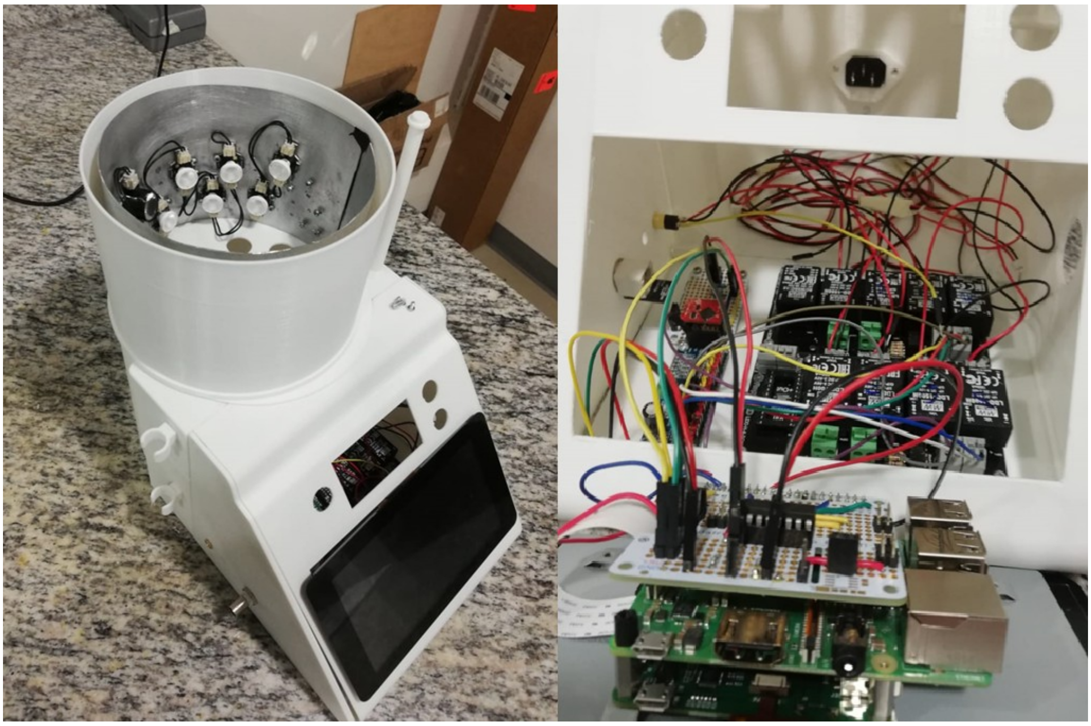


Figure 30. Construction of the Photo Reactor

Figure 31. Raspberry Pi Photo Reactor

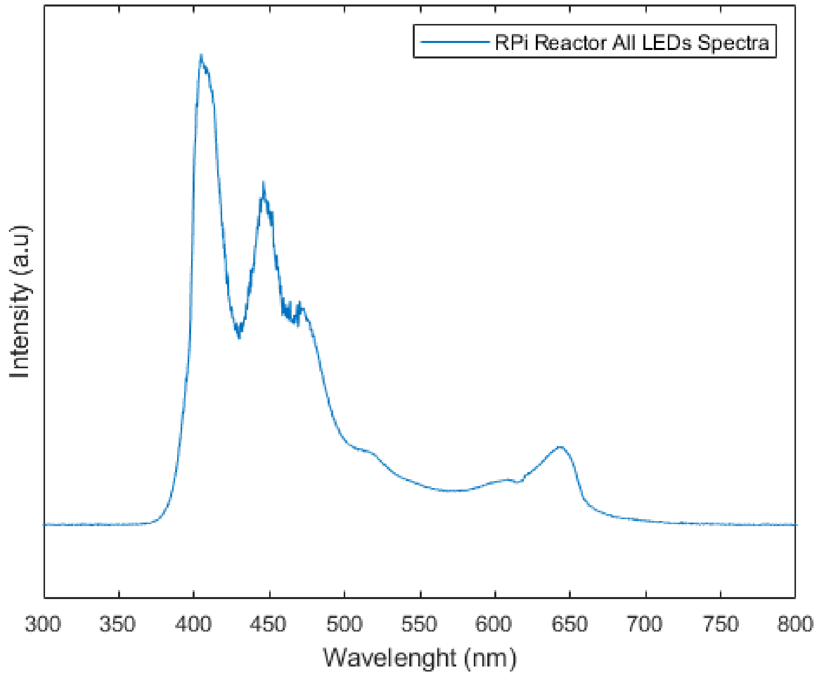


Figure 32. Spectral wavelength of the RPi reactor ALL LEDs

Light intensity measurements

Table 7: Light intensity values of the light sources

Light Source	**Lumen/m2**
RPi FULL LEDS	9804
RPi RGB LEDS	9201
Rpi BLUE UV LEDS	10122

COBS Reactors UV-VIS absorption spectrum

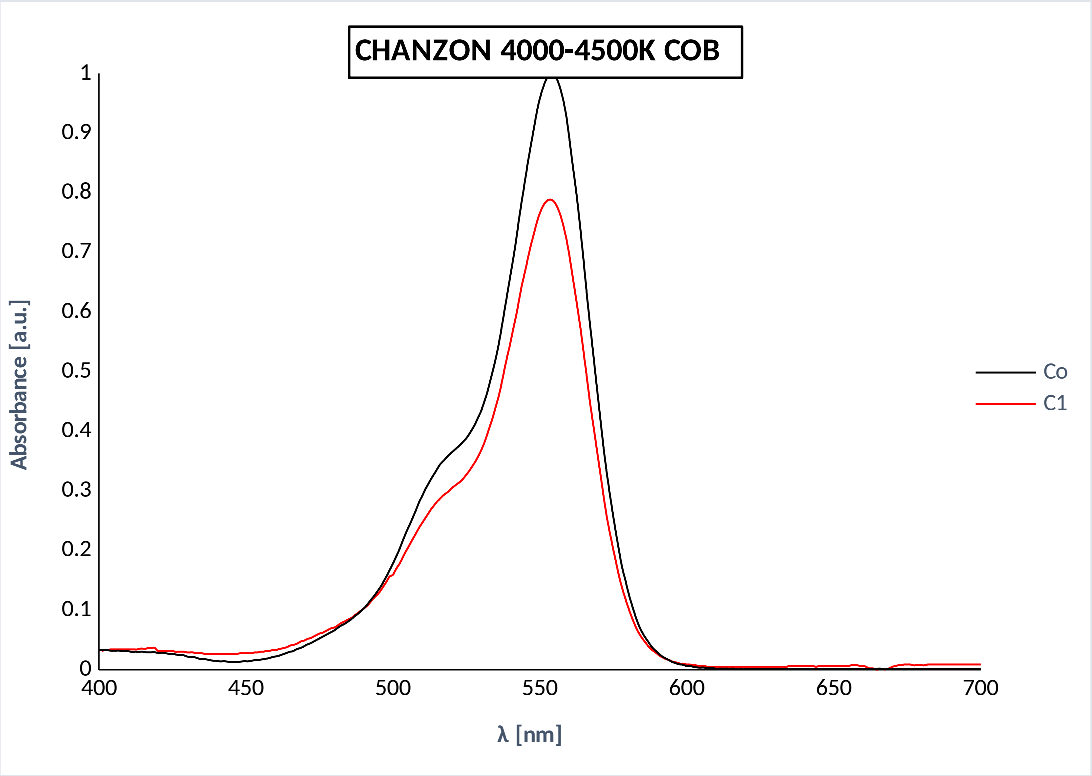


Figure 33. UV-VIS absorption spectrum of CHANZON 4000-4500K COB

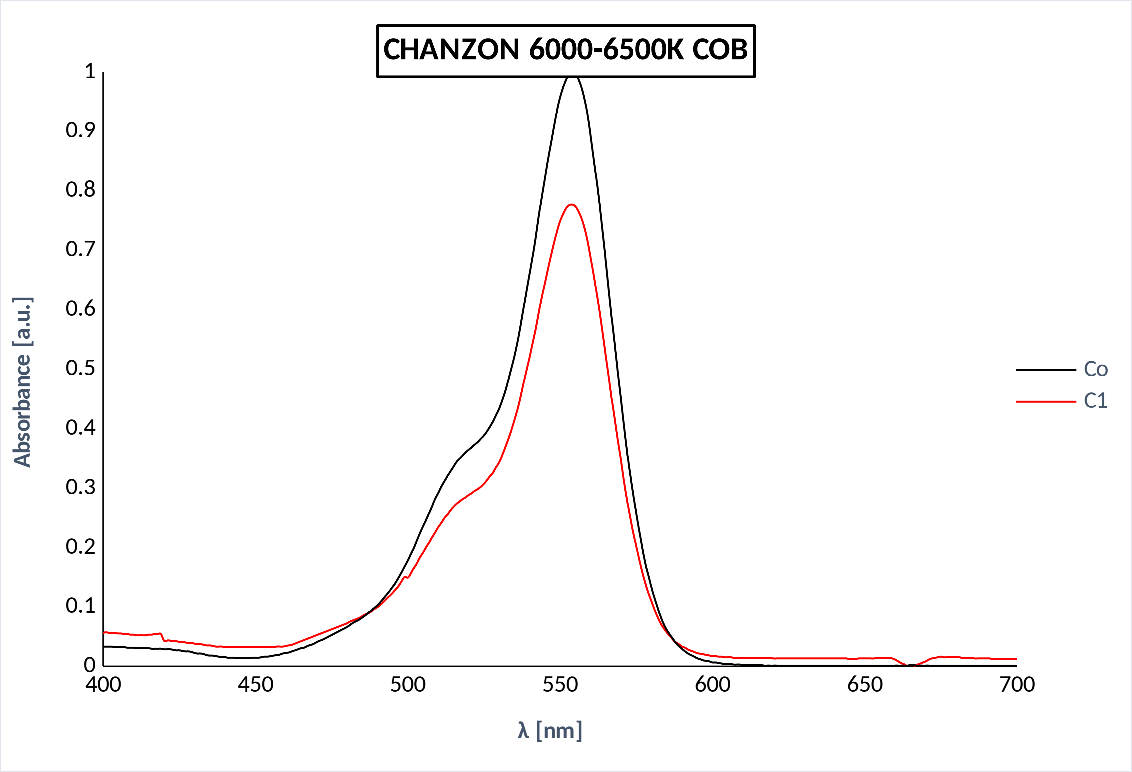


Figure 34. UV-VIS absorption spectrum of CHANZON 6000-6500K COB.

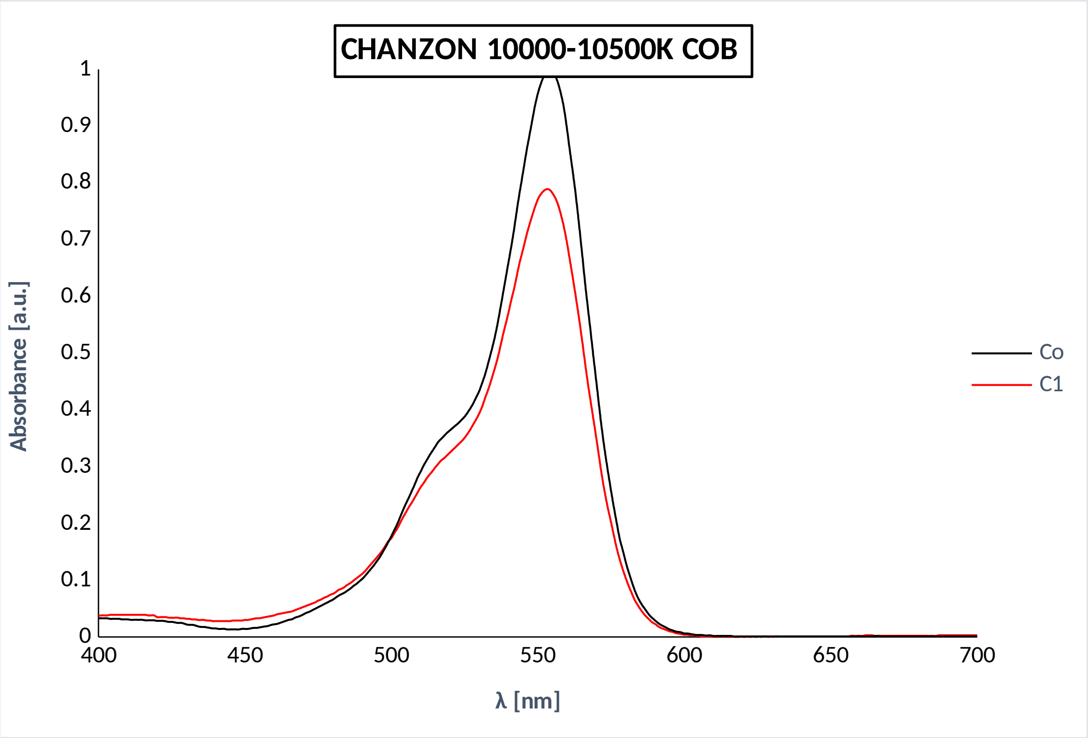


Figure 35. UV-VIS absorption spectrum of CHANZON 10000-10500K COB

LED Reactors UV-VIS absorption spectrum

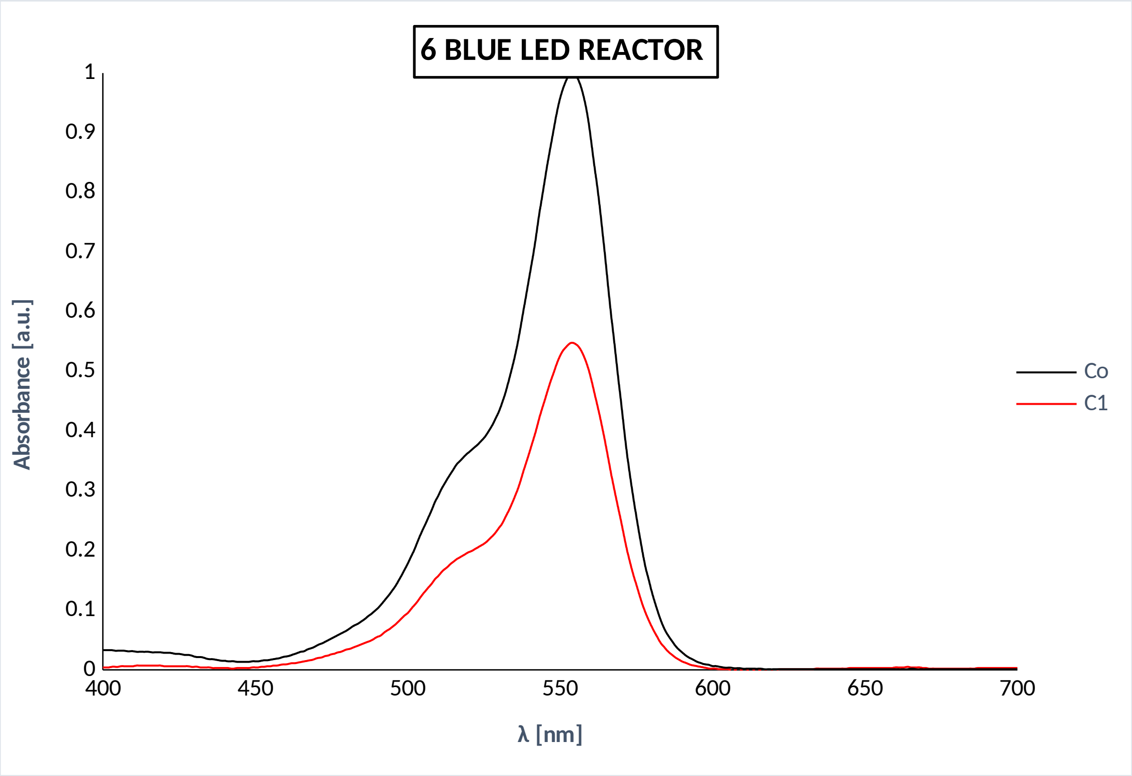


Figure 36. UV-VIS absorption spectrum of BLUE LED Reactor

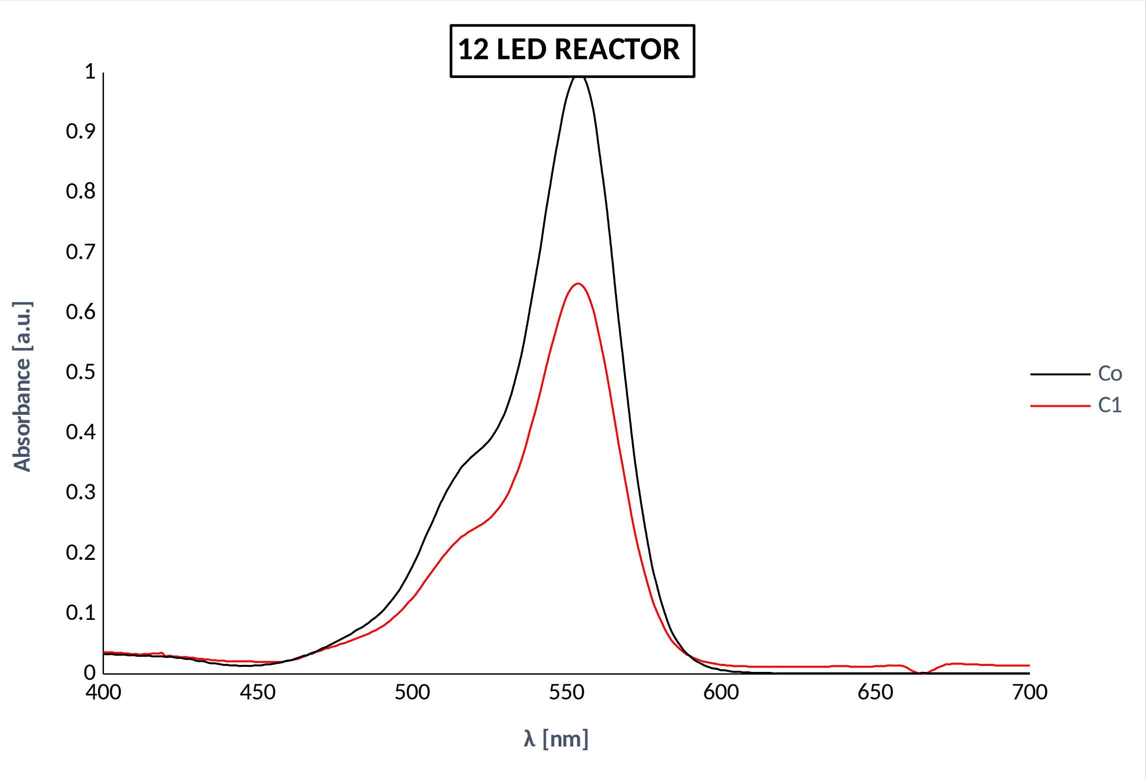


Figure 37. UV-VIS absorption spectrum of 12-LED Cree Reactor

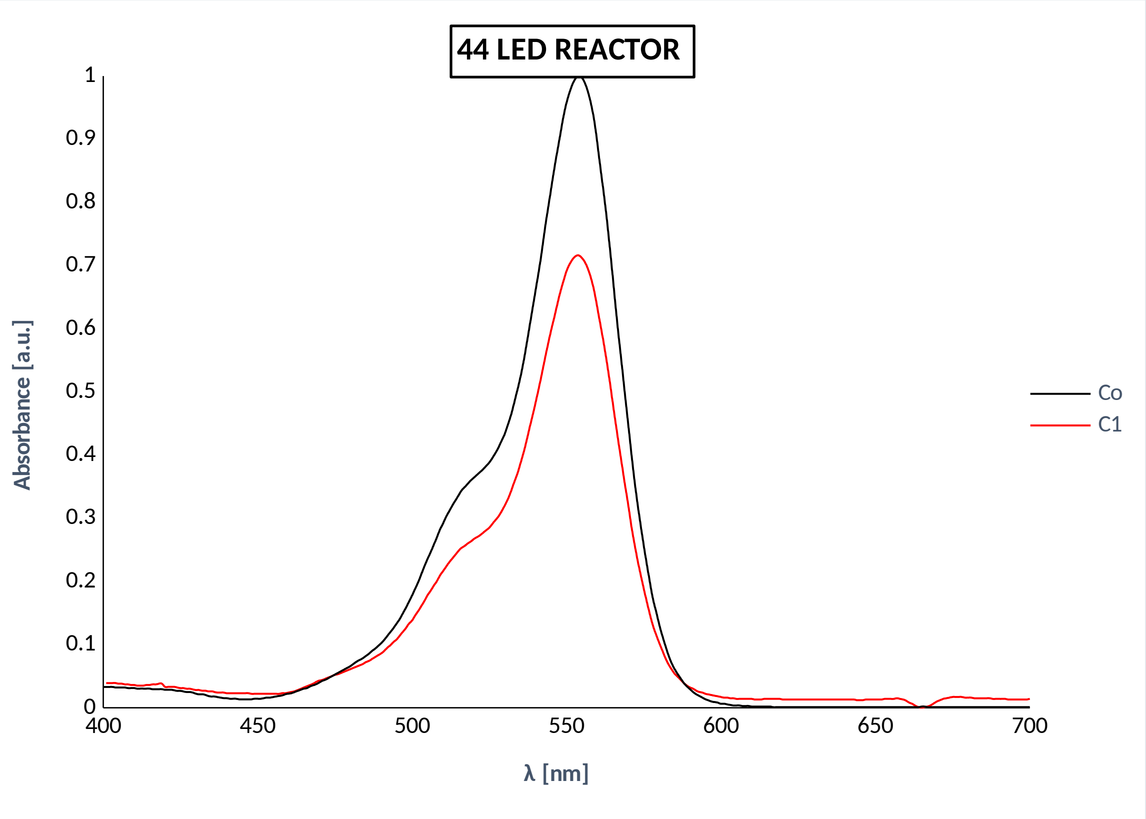


Figure 38. UV-VIS absorption spectrum of 44 LED Reactor

KESSIL reference light source UV-VIS absorption spectrum

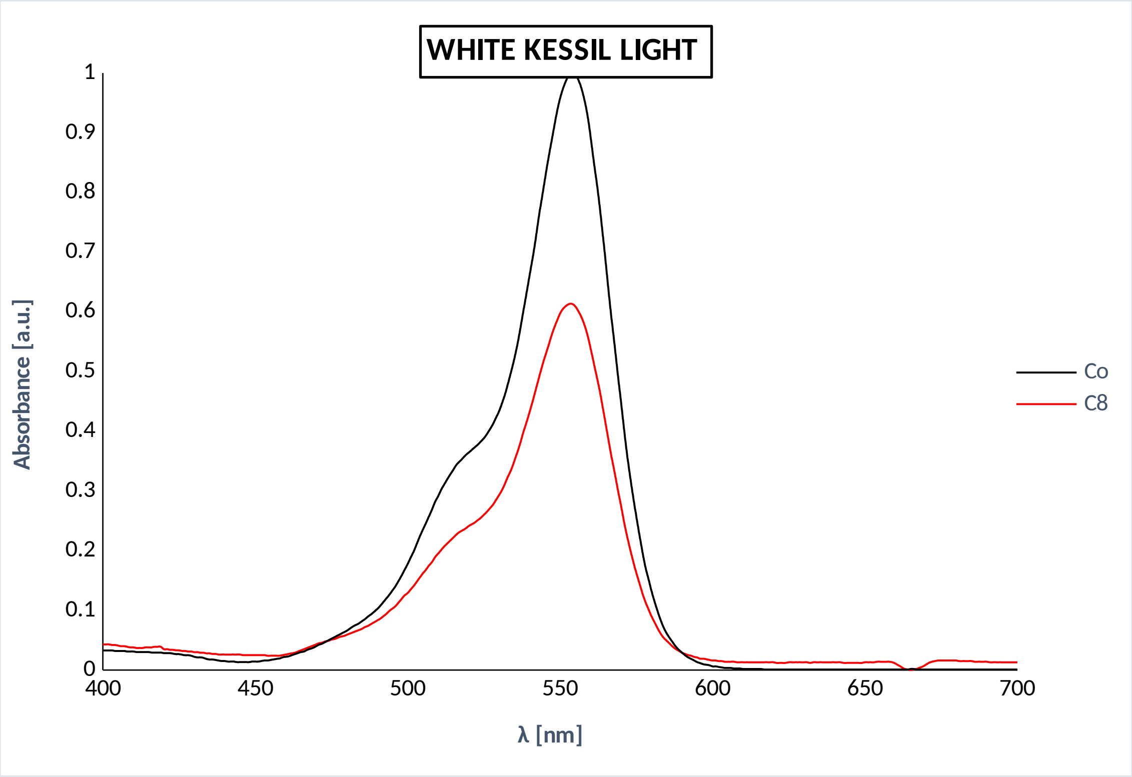


Figure 39. UV-VIS absorption spectrum of WHITE KESSIL LIGHT

KESSIL Reference light source

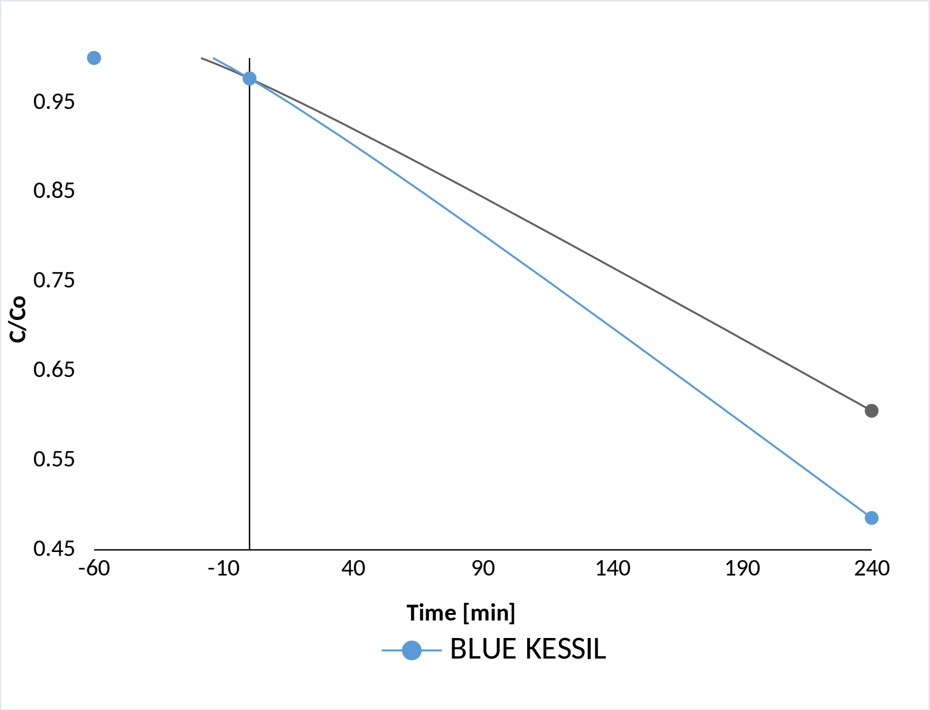


Figure 40. Photo Catalytic degradation of Rhodamine B as a function of irradiation

COB Photoreactor

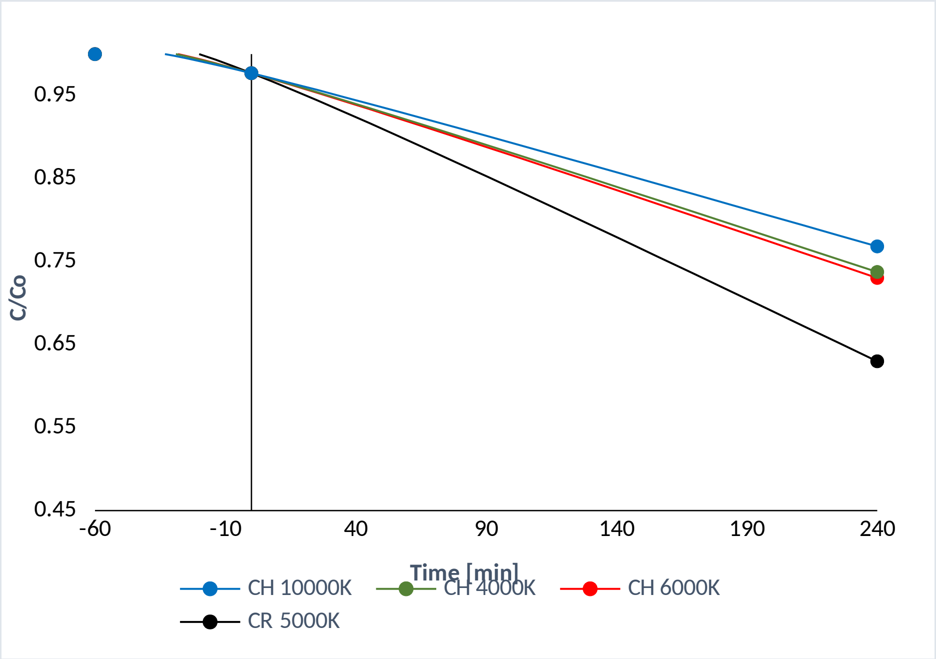


Figure 41. Photo Catalytic degradation of Rhodamine B as a function of irradiation time.

LED Photoreactors

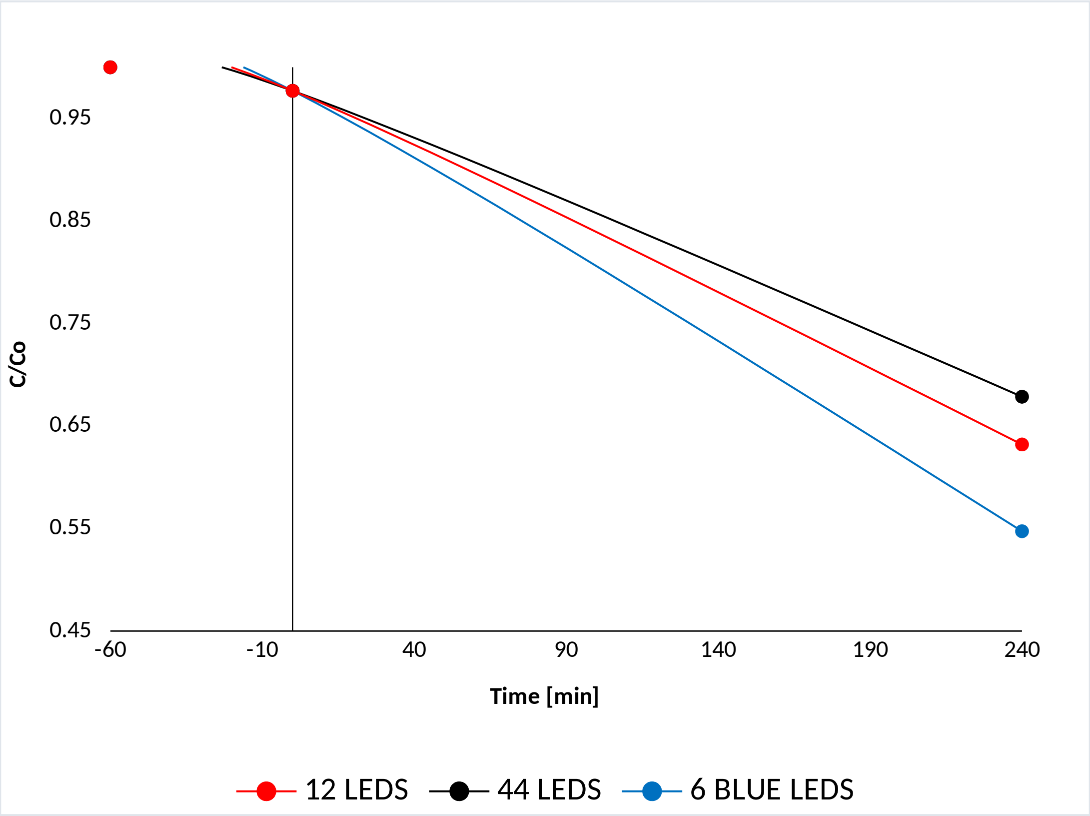


Figure 42. Photo Catalytic degradation of Rhodamine B as a function of irradiation

time.

Table 8. List of cost of the materials used in the Raspberry Pi Photoreactor.

Component	**$Price**
Raspberry Pi 3B+	70.00
7’’ Touch Screen	65.00
Perma Proto board Pi HAT	8.50
Perma Proto borad mint	5.50
Female and male jumper cables	7.00
Female and male pins	4.00
PCA9685 board	9.50
LDD DC-DC Drivers x7	80.75
EZO Integrated circuit	40.00
Atlas Scientific pH probe	50.00
Cree High power LEDs	69.30
Al structure	2.00
Arctic fan	7.00
Nd magnets	1.50
PWM speed controller display	12.50
L293D motor	5.60
LM2695 coverter	3.40
Peristaltic pump	5.00
DS18B20 sensor	8.50
3D printed structure	220
SD Card 32 Gb	15.00
Polycarbonate filament	45.00
Total	**734.25**