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An approach to the utilization of artificial high power LED UV-A radiation in photoreactors for methylene blue degradation

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Utilization of UV LED light is a trending in the development of photoreactors for pollutant treatment. In this study, two different geometries were studied in the degradation of Methylene Blue (MB) using high power UVA LED as a source of light. The dosage, initial concentration, electric power and H₂O₂ addition were evaluated in two geometries: a mini CPC (cilindric Parabolic Colector) and a standar batch reactor with external irradiation. Best degradation was obtained for 0.3 g/L TiO₂, 40min and 15ppm of MB of initial concentration in the standard batch reactor. It was found that the best system was a cpc geometry. Also, peroxyde hydrogen was used as electron acceptor and it was obtained 97% degradation in 30 min with 10mM H₂O₂ and 0.4gTiO₂/L. Power of the LEDs was also evaluated and it was found that 20W/m² is the best operational condition to achieve the best MB degradation avoiding oxidant species recombination.

Introduction

Methylene blue is an aromatic heterocyclic chemical used in the medicine as antiseptic, skin healing, and fungicide in aquaculture. In addition, it can be used for the microscopical bacteria tanning, and dyeing cotton, silk and wool (Fig. 1).

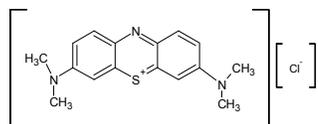


Fig 1. Structural form of methylene blue.

Around 15% of worldwide dyes used for textile processing are liberated in wastewaters, causing pollution in aquatic ecosystems¹. This molecule is recalcitrant to solar photolysis, which makes necessary to explore new process to eliminate the dye content in industrial wastewater. Advances Oxidation Process AOPs are an alternative for high recalcitrant substances degradation. Heterogeneous photocatalysis is promising AOPs for recalcitrant wastewater treatment. This technique is based on the direct or indirect absorption of visible or UV light by a semiconductor, in particular TiO₂. In the Surface of the semiconductor takes place the redox reactions by the electron-hole pair photogenerated².

As an alternative to solar light, the development of photoreactors using artificial light such as LED (Light Emitting Diodes) are being developed³. UV-LED are a safer alternative to halide and mercury lamps, energy more efficient as a source of photons (by only requiring between 6 and 28 watts of

electricity depending on the amount of lumens), and about 100 times long-lasting life⁴⁻⁶. Fluorescent lights require between 40 and 150 watts, and they are far more fragile and less portable.

LED photoreactor are being used in the homogeneous and heterogeneous catalysis⁷. Table 1 summarizes the some studies for photodegradation of dyes from textile industry.

Table 1. Photoreactors LED used for dye degradation.

Type of photoreactor	LED Power	dye	Description
Batch cylindrical 125 mL	8 mW /cm ² 30 LED 350 nm	Methylene blue, malachite green, direct blue-15, amarant.	95% Degradation / 4h TiO ₂ immobilized in mosquito netting. Evaluated number of LED and H ₂ O ₂ addition ⁸ .
Batch 200 mL	39 mW/cm ² 405 nm and 73 mW/cm ² y 450 nm	Methylene blue phenol red and methyl red.	100 % Degradation / 3h CdS Microspheres Glucose addition to avoid photocorrosion ⁹ .
Continuous photoreactor with three impregnated pipes with TiO ₂	15 LED UV 390-410 nm	Methylene blue, Rhodamine B and malachite Green.	100% Degradation / 100 min Alkaline condition benefits degradation ¹⁰ .
CSTR system	40 W/m ² 96 LED UV-A	Reactive black 5	89% Degradation / 10 h

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	375nm		TiO ₂ Degussa P25 ¹¹ .
Batch 125mL	8 mW/cm ² 30 LED 350 nm	Direct Blue-15	90% Degradation / 3h
			TiO ₂ Nanoflowers are better than nanotubes and nanospheres ¹² .
Batch 150 mL	60mW UVLED 390-410nm	Rhodamine B	99% Degradation /120 min
	50mW BLED 430-505nm		Best photocatalyst BiOCl with UV LED ¹³ .
	50mW GLED 525-570nm		
	50mW RLED 630-660 nm		
Batch 110mL	23 W/m ² 96 LED UVA 375 nm	Reactive Black 5	100% Degradation / 40 min
	85 W/m ² 12 LED 365 nm		85W/m2 LED UVA are better than solar radiation ¹⁴ .
Batch with immobilized catalyst on the walls	6 LED UV 385 nm	Direct Red 23	97% Degradation / 30 min
			Addition of S ₂ O ₈ ²⁻ improves photooxidation ¹⁵ .
Batch 125 mL	5 LED UV 390-410 nm	Rhodamine B	100% Degradation /180 min
			Addition of H ₂ O ₂ enhances oxidation, but metal addition decrease the oxidative process ¹⁶ .

Although there are studies with several cylindrical and parabolic geometries, it has not been compared with a small CPC to conclude the feasibility of using this UVLED with this geometry instead of solar light.

The particular case of study will be the Methylene Blue degradation, which occurs as shown in Fig 2. The route goes by the N-dealkylation of auxochromic alkylamine groups. At the end the MB is transformed in H₂O, CO₂ and other inorganic molecules^{17,18}.

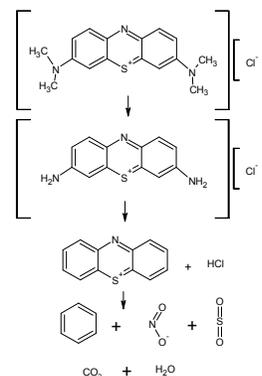


Fig 2. Pathway of MB degradation.

In this study, the viability to use UV-LED as source of light in the MB degradation using heterogeneous photocatalysis with TiO₂ was evaluated. Two different geometries: a mini CPC (Compound Parabolic Collector) and a cylindrical batch UVLED illuminated reactor were compared.

Experimental

Photocatalyst and chemicals

It was used methylene blue three hydrated (CAS 7220-79-3) Duksan pure chemicals Co., Ltda. As catalyst titanium dioxide (AEROXIDE TiO₂ P25) and deionized water. Air from a compressor was used to supply the enough dissolved oxygen in the photoreactor.

Photoreactors

System A: The photoreactor comprises a 1 L pyrex vessel 10cm diameter illuminated externally with an effective volume of 500mL. 4 LED of 30W TY-365nm30W High Power Ultra Violet (395-495nm) each were placed in opposite sides (30-36V DC, 0.7-1.0A for all 4 LEDs plugged in parallel) with a viewing angle 115-125 degrees and output optical radiation of 900-1200 mW per LED.

System B: The photoreactor comprises in a miniCPC of 4 pyrex tubes, with 2 cm outer diameter, 11cm long, connected to a 2L vessel with an effective volume of 600mL. The system used a centrifugal pump from washing machine. On the top of the pyrex tubes was placed the LED-UV light source. For both system the LEDs-UV were adapted with small PC fan at 12 V to avoid overheating. Power supply was done using EXTECH instruments 382280 (Fig 3) and the intensity of irradiation was varied with the amperes supplied to the LEDs at 30V.

For both systems, each LED consumed no more than 0.2A at 30VDC to give an irradiation output of 30W/m². Irradiation was about 1.2W per LED and electrical consumption was about 6W, which led to an optical efficiency of ca. 20%.

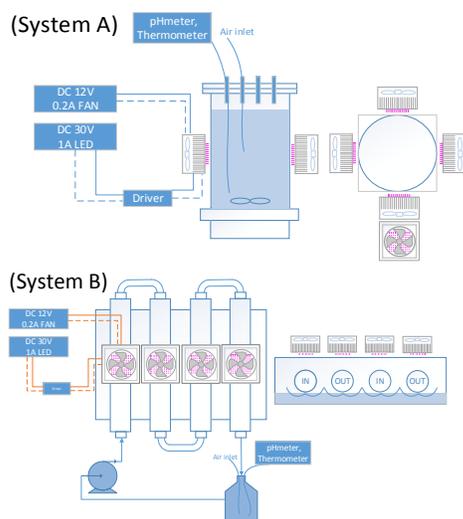


Fig 3. System A: Scheme of the batch photoreactor. System B: miniCPC scheme photoreactor.

The MB concentration was measured using Spectroquant Pharo 300 Merck spectrophotometer at 660 nm using 10 mL of sample. Dissolved oxygen and pH was monitored using a multiparameter Orion 4Star. UV-A irradiation was measured for each LED using a radiometer Delta OHM HD 2102.2 UV-A at a distance of 1cm from the LEDs. Photocatalytic degradation was normalized using C/C_0 , where C_0 and C are the initial and final concentration of the dye, respectively. Mineralization of MB was measured with Total Organic Carbon Shimadzu TOC-V-CPH.

Operational Conditions

All solutions were prepared with deionized water, at normal pressure and temperature. Air flowrate was *ca.* 0.5 L/min to provide enough dissolved oxygen and promote the mixing in the vessel. The System A operated at 200 rpm ($Re > 30000$), and the System B at 8.6 L/min ($Re > 15000$). The reactive volume used was 0.6 L; 10mL of aliquots were taken to follow degradation.

Experimental procedure

First it was established the amount of catalyst that presented best degradation (catalyst load), keeping initial MB concentration constant. The amount of catalyst was varied from 0.2 to 1.6g TiO_2/L and from 5 – 20 ppm of MB. The best amount of catalyst load was selected for each system for the rest of the study.

After catalyst amount was selected, initial MB concentration was changed with 4h of reaction. Finally, the electrical power of the light system was evaluated using the best catalyst load and initial MB concentration. The pH was 7.1 to promote good adsorption onto the catalyst (cationic dye). The reactor was closed and was maintained in a dark period to allow equilibria adsorption.

Results

Catalyst load effect. Fig 4 shows best results obtained in the MB degradation at 15ppm of initial concentration for 2h of reaction. Results show that over 0.4g TiO_2/L there is a decrease in the MB degradation, which may be related to the screening effect of the solution for the System A. In the other hand, System B allowed superior catalyst load showing a greater light penetration into the pyrex tubes.

It suggested System A is able to reach same photodegradation using less amount of catalyst being more efficient in the light utilization than System B.

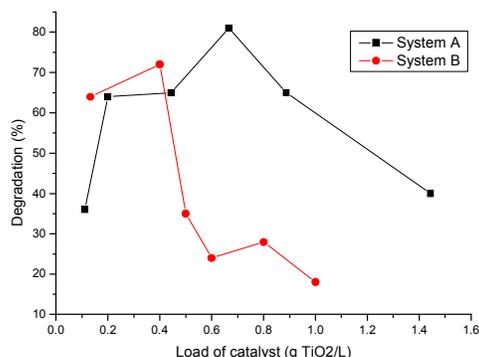


Fig 4. Catalyst load vs. degradation percentage. 10 ppm MB, Power 30 W/m^2 .

It has been reported that even at dosages about 1.0 g/L of TiO_2 there is no screening effect in the photocatalytic effect¹⁹. In the other hand, loads over 1.5g TiO_2/L , has been reported as inhibitory in the light utilisation due to the overshadow generated in the solution⁷. This geometry found a catalyst dosage lower, which may be related to the geometry of the photoreactor, source of light, and the pyrex diameter. For the rest of the study, it was selected the best of the catalyst weight in order to operate at optimal conditions.

Methylene blue initial concentration effect. Initial MB concentration was evaluated between 5-20ppm using the best TiO_2 dosage in each system (Fig. 5 and 6). Results show that higher MB concentration decreases the degradation reached at one similar time. It may suggest inhibition in the transfer of photons to the catalyst due to an increase in the absorbance of the substrate as it turns dark blue.

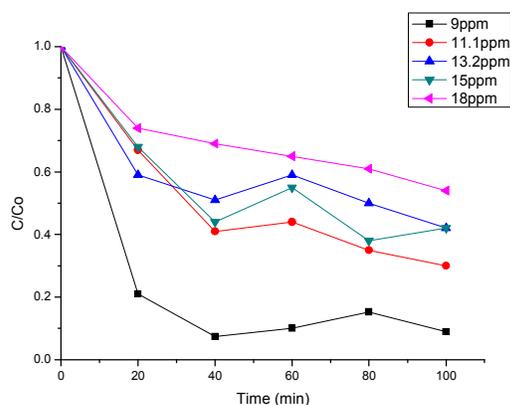


Fig 5. Degradation of MB for system A. Irradiation Power = 4LEDs at $30\text{W}/\text{m}^2$.

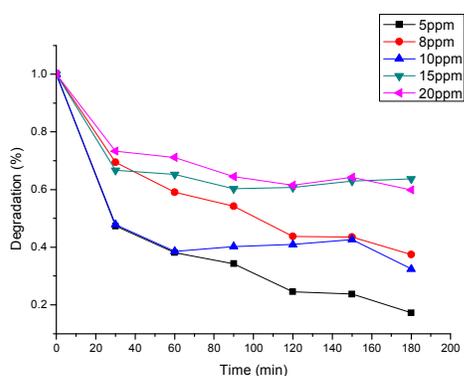


Fig 6. Degradation of MB in system B. Power = 4 LEDs at $30\text{W}/\text{m}^2$ power.

Assuming negligible volume in the connecting lines, a perfectly stirred tank and the reaction occurring only in the reactor volume, the mass balance of a batch-recycle reactor can be written as:

$$\int_0^{V_R} r dV_R = \frac{d}{dt} \int C_R dV_R + V_T \frac{dC_T}{dt} \quad \text{Eq (1)}$$

Where V_R is the illuminated reaction volume, V_T the liquid volume in the tank, and r the reaction rate. Considering no spatial dependence of C_R and small differences in the entrance inlet and outlet concentration $C_R \approx C_T$:

$$r = \frac{dC_T}{dt} \frac{V_T + V_R}{V_R} = \frac{1}{\theta} \frac{dC_T}{dt} \quad \text{Eq (2)}$$

With θ being the dilution factor of the photoreactor (illuminated – total volume ratio). Photocatalytic degradation can be written by Langmuir-Hinshelwood rate equation, Fig 3, as follows:

$$r = \frac{\theta k K C}{1 + K C} \quad \text{Eq (3)}$$

Where C is the concentration of MB, k the specific reaction velocity and K the equilibrium adsorption constant. Integrating equation 1:

$$\ln \frac{C}{C_0} = -\theta k' t \quad \text{Eq (4)}$$

Being k' the apparent pseudo-first-order rate constant and t the reaction time.

In Table 2 it is shown the apparent kinetic constant for different initial concentration at the best catalyst load on each system. It can be seen photocatalytic degradation is enhanced by the low MB concentration, with System B being 1.8 times faster than System A at an initial MB concentration of ca. 8 ppm. In spite of the higher specific velocity of reaction in the system B, the evolution of the MB degradation is seen faster for system A (Fig 5-6) due to the lack of dilution of the reactive volume. However, the lower specific velocity of reaction of system A may be related to a low light penetration of the vessel. This is enhanced in system B where the light has an optical path of less than 2 cm.

Table 2. Effect of initial MB concentration in the oxidation.

Initial MB concentration (ppm)	$k' (10^{-2} \text{ min}^{-1})$	
	System A ($\theta=1$)	System B ($\theta=0.22$)
5	--	6.51
9	1.82	--
8	--	3.41
11.1	1.13	--
10	--	2.26
13.2	0.67	--
	--	2.19
15	0.84	--
20	--	1.75
18	0.53	--

Supplied Power effect: Fig. 7 and 8 shows the effect of decreasing the exposed area to the irradiation turning off 2 of the 4 LEDs at the best initial concentration and catalyst dosage. It was found no significant differences between the decreases of MB concentration when area of illumination decreased to the half. It may be possible that 4 LEDs of $30\text{W}/\text{m}^2$ may be more than the system could exploit from the configuration for both systems. It means kinetics become independent of the irradiation field, which means an order zero to the irradiance field and unnecessary energy consumption²⁰.

It is well known that the solar photoreactor look for the concentration of light in order to achieve better photodegradation of pollutants, but in this case, both geometries are over irradiated, and so chemical reaction may be on its maximum velocity of

reaction at this point of operation. Even though, geometry was a determinant factor for an appropriated light harvesting, being the batch system A the best one.

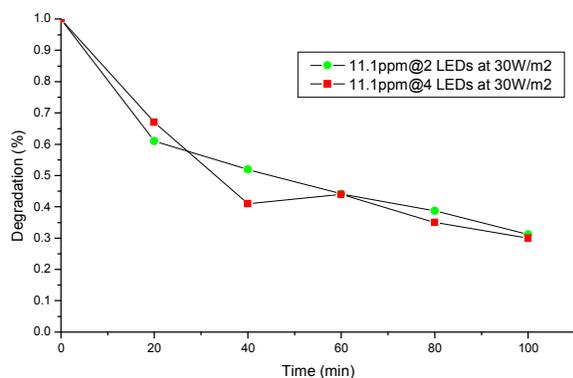


Fig 7. Comparison of the irradiation flux for the system A.

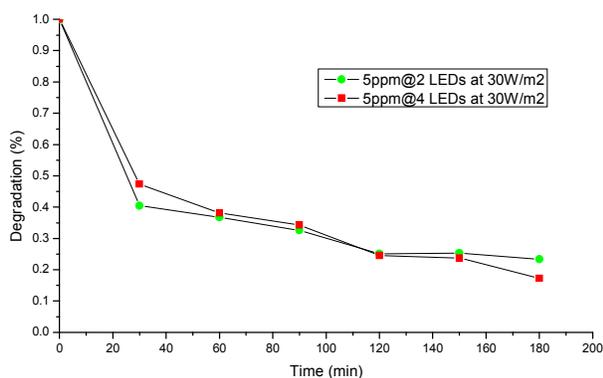


Fig 8. Comparison of the irradiation field for the system B.

Effect of peroxide addition and the power. Hydrogen peroxide is well known as electron acceptor in the redox reactions on the semiconductor surface creating more hydroxyl radical empowering the degradation kinetics²¹. Even though, the excess of illumination led to low MB degradation, suggesting a competitive reaction with oxidant species. Fig 9 shows that over 20 W/m² the efficiency of the MB oxidation drops from 97% to 74%. It could be related with recombine process of hydroxyl, perhydroxyl or electron-hole pairs on the semiconductor¹⁸.

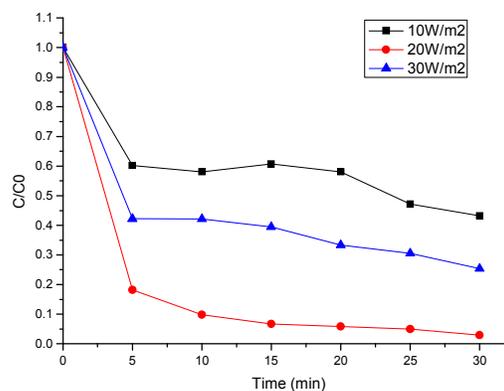


Fig 9. Peroxide addition with different power irradiation. 5 ppm MB, 0.3 g/L TiO₂, 10 mM H₂O₂, system B.

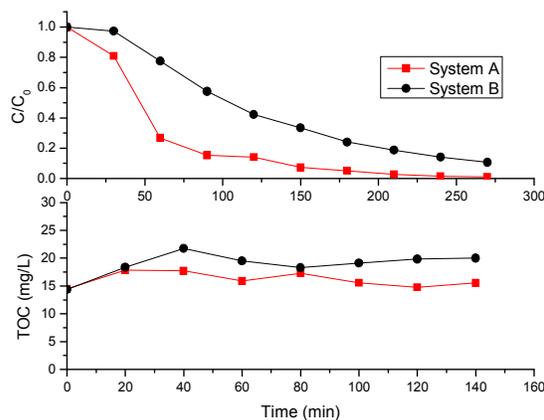


Fig 10. Mineralization of MB with hydrogen peroxide addition. 20 ppm MB, 10mM H₂O₂, 20W/m² with 4 LEDs and best load for each system.

Decolorization is the first step in the degradation of inks. According to the results in Fig 10, although more than 80% of MB degradation was achieved at 180 min (Fig 6), not all the mineralization process was achieved during the photocatalytic oxidation. An optimization has to be done in order to achieve the lower energy consumption not only to the high UVLED power but also to scavenger concentration. Despite the low of mineralization, system B resulted in a higher specific rate of reaction. This would be a better configuration to take advantage or artificial LED irradiation than system A. However, dilution factor (θ) has to be increased closer to the unit in order warranty a total volume illuminated and to reduce the slow decrease of the MB concentration in the cpc system.

Compared to other lamps and solar systems, UVLED photoreactors may be a suitable option not only for MB degradation but also for other types of pollutants. Although CPC reactors has been the geometry most appropriated to harvest the solar photon flux it may

be possible to distribute the radiative field in different geometries for LED UV arrays. In that case, no need of concentration of light may be necessary with focused LED UV light. Then simpler and homogeneous flat plate UV photoreactor may be an option that benefits optical path and maintenance of the reactive system. In contrast, other authors had been able to degrade this dye but with higher times of operation. It is shown in Table 3 the comparison with other studies using MB and TiO₂/UVLED.

Table 3. Comparison of several studies of MB degradation with LED UV-vis photoreactors.

SYSTEM	CATALYST / LIGHT SOURCE	DEGRADATION / TIME	MB degraded (g / g.h)
Multipass quartz tube reactor	TiO ₂ supported on quartz tubes / 15 UV-A LED 12mW	100% / 300 min ²²	1.7
Submerged cylindrical LED UVA	TiO ₂ -immobilized / UVA 8mW/cm ²	95% Degradation / 4h ⁸	1.7
Cylindrical batch	CdS / UVA LED 25W	100% Degradation / 3h ⁹	18.5
Coupled UV Lamp+visible LED array	0.5 mW/cm ² Visible LED / Ni-TiO ₂	45% / 180 min ²³	92.6
Cylindrical batch	LED visible / 20W / Ag ₃ PO ₄ /ZnFe ₂ O ₄	90% / 60 min ²⁴	8.3
Petri Dish	BLUE LED / 3 W / PDMS-TiO ₂	73% / 8 h ²⁵	20.8
Petri Dish	WHITE LED / 3W / BaFe ₁₂ O ₁₉	70% / 360 min ²⁶	111.1
Cylindrical Cell	UVLED / 3W / m-TiO ₂	90% / 120 min ²⁷	16.7
This study	UV LED / TiO₂ / 20W/m²	99% / 30 min	119.0

Conclusion

It was evaluated two different geometries of the photoreactors and it was enhanced the degradation of MB using high power LED UV-A in a local fabricated photoreactor. Two geometries were evaluated: miniCPC (Cylindrical Parabolic Collector) and vertical cylindrical with external irradiation both coupled with LED UVA. Best configuration was the CPC because of its ability to concentrate radiation and low optical path although is required a lower dilution factor to avoid non-reactive dark volumes. Thus, it was evidenced that the LEDs are an effective source of light for photocatalytic reactions. Peroxide Hydrogen addition resulted in an increase in the photocatalytic treatment, but excessive UV from LEDs inhibited MB degradation. Further examination is required in

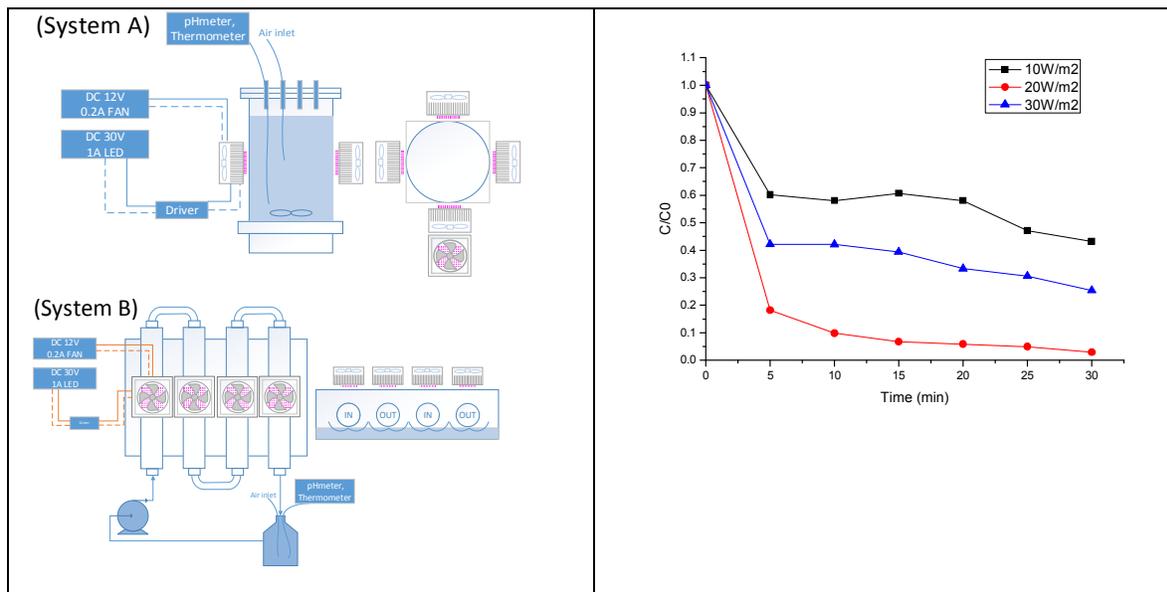
order to find the optimal operation conditions that could reach the high kinetic behavior at low energy consumption.

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A Two laboratory photoreactors compared in the MB degradation using high power UV LED resulted in more than 98% degradation.