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Enhancing Photon Transfer Efficiency in Photocatalysis Using Suspended LED Lights for Water Treatment

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Abstract: Photocatalysis application in water treatment has been the object of many researchers worldwide in recent decades. However, there are limited commercial applications due to low photon transfer efficiency, which create barriers leading to challenges in making the process efficient and economically feasible. Fixed UV/visible light sources, which are generally located outside the reactor or encapsulated in quartz tube inside the reactor are the source of energy to activate photocatalyst generating powerful oxidants such as electrons and holes. Suspended waterproof LED visible lights were employed to enhance photon transfer efficiency. Consequently, the required energy was lower resulting in negligible temperature increase and eliminated the need for an external cooler, no need for quartz (UV transparent) or treated glass reactors, enhanced mixing due to continuous movement of light bulbs by convective currents, and minimum/no attenuation. Direct Blue 15 (DB15) dye was used as model compound and the photocatalyst was P25 TiO_2 (Average particle: 30 nm, Surface area: 50 m^2 g^{-1}). The samples taken at different time intervals were analyzed by UV-Vis. spectrophotometer (UV-3600), and TOC-V CPN total organic carbon analyzer (both from Shimadzu). It was found that for the same level of degradation, the degradation rate increased by about 50% compared to conventional fixed light photoreactor. Overall, the cost of the operation can be reduced substantially, paving the road for feasible commercialization of the process.

Keywords: photocatalysis; photon transfer efficiency; suspended LED lights; water treatment

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1. Introduction

World population is steadily increasing, and the need for clean water has never reached to its existing level. Heavy agricultural and industrial activities have resulted in release of different contaminants to aqueous matrices with negative ecotoxicological impacts worldwide, increasing the pressure on finding safe feasible treatment methods for contaminated water/wastewater resources. There are several treatment methods where macro pollutants are removed by conventional processes, while organic micropollutants, viruses and pathogenic bacteria may survive these processes and therefore additional removal processes are required [1]. Advanced oxidation processes (AOPs) have been extensively employed mostly as a tertiary treatment method in removal of organic pollutants from water/wastewater. Among AOPs, photocatalysis is among the most researched process, where ultraviolet (UV)/visible light is used as a source of energy to excite photocatalysts, leading to generation of hydroxyl radicals (OH*), which can easily mineralize organic compounds. Photocatalysts are semiconductors such as titanium dioxide (TiO_2) or Zinc Oxide (ZnO), and TiO_2 is the most desirable photocatalysts as it is a stable, non-toxic, cheap semiconductor with an energy band gap of 3.2 electron volt (eV) [2]. This energy band gap can be overcome by ultraviolet (UV) light so that electrons can get enough energy to leave the valence band and reach the conduction band, leaving holes that can react with water and produce OH*. Visible light with about 3% UV does not provide enough energy for excitation of TiO_2, and the fast recombination of electrons and holes make the use of visible

light inefficient. However, TiO_2 lattice can be doped by metallic elements which reduces the band gap sufficiently, enabling use of visible light [3].

Quartz glass (which is transparent to UV) is used when UV light is needed, while regular glass is preferred for visible light (where doped photocatalyst is used), which is quite cheaper than quartz glass. Light attenuation (specially in slurry reactors), fouling, high energy requirements, mass transfer limitations, and long residence time are some of the challenges, which decrease photons transportation and degradation efficiency and increase the overall cost of the process.

In almost all experiments UV/visible lamps were located either out of the photocatalytic reactor or placed inside fixed transparent quartz tube casing (UV transparent) in the reactor, and in all of them the light sources were stationary. Visible/UV light must reach the photocatalyst inside the reactor, and as such significant portion is reflected and/or absorbed by the transparent reactor wall. In large reactors, the light may travel several meters to reach the suspended photocatalyst particles inside the reactor and photons may be lost due to attenuation. To overcome this barrier, high energy light sources are used, which not only increase the cost but also conversion of the lost energy to heat leads to temperature increase inside the reactor and therefore a cooling cycle is required to keep the temperature of the reactor at the desired level. Despite substantial research in photocatalysis, commercial application of the technology is still limited to processing challenges such as low efficiency, and cost. One of the challenges is design and development of photocatalytic reactors with low mass transfer resistances, high photon transfer efficiency, and lower cost [4].

Many photocatalytic reactors such as Swirl reactor [5], spinning disk reactors [6], monolith reactors [7] and micro-reactors [8] have been developed to enhance mass transfer. Research to increase photon transfer is an important topic in photocatalytic oxidation. Photon transfer efficiency can be increased by increasing the illuminated surface area per unit volume of the photocatalytic reactor. Many reactors have been used to enhance photon transfer efficiency, some of which are slurry reactors (2631–170,000 m^2/m^3), annular reactors (27–2700 m^2/m^3), optical fiber reactors (46–2000 m^2/m^3), monolith reactors (900–1300 m^2/m^3), spinning disk reactors (50–66,000 m^2/m^3) and microreactors (7300–250,000 m^2/m^3) [9].

To overcome the challenges, the fixed UV/light sources can be replaced by suspended, battery operated LED light bulbs, which has the potential of revolutionizing the process with substantial cost reduction and cab be advantageous to global problem of access to clean/drinking water. In an attempt in 2015, wirelessly powered ultraviolet light emitting diodes were used for photocatalytic oxidation of methylene blue in water. The light emitting diodes were distributed inside the reactor at fixed positions, consequently, 30% higher removal rate of methylene blue was achieved [9]. Floating ultraviolet LED lights were used for water purification, where the UV lights were attached to a floating system remaining at the water surface, while the UV lights are under water surface. In the patent associated with this system, the inventors claimed higher efficiencies for water treatment in multiple ways [10]. Table 1 represents some of the reactors in lab scale and the required energy.

In this study, miniature battery-operated waterproof LED lights are introduced to the photocatalytic reactor. The total energy used by the lights in the reactor is 1.7 W and assuming that a maximum of 15% of that wattage would be in the UV range, it clearly shows that the energy requirements is much lower compared to UV lamps. The available LED lights in the market has a density very close to that of water and with minimum adjustment they become fully suspended in water. The adjustment has negligible impact on the size and shape of the LED lights. Since the light source is suspended it can move easily inside the reactor with convective current imposed either by water circulation or a mixer. Therefore, the light can reach easily to the photocatalyst and consequently the photon transfer efficiency will be enhanced. Clearly, the photocatalysts can be activated easily as the moving lights, which can cover every corner inside the photoreactor produces electrons and holes for the degradation of organic contaminants. Compared to traditional reactors, the penetration distance for the photons to reach the photocatalyst would be much

shorter (a maximum of 2 inches). Obviously, it reduces attenuation and since the light sources are moving constantly inside the photoreactor, there would be negligible fouling. The enhanced photon transfer efficiency reduces the residence time, and therefore smaller photoreactors are required to achieve the desired level of degradation.

Table 1. Power requirements in photocatalytic reactors.

Reactor Shape, Volume, mL	UV/Visible Light Source Wattage, Watt	Watt per Unit Volume W/mL	Reference
Cylindrical 100 mL	200 W high pressure mercury lamp	2	Yao et al., 2023 [11]
Dish type 100 mL	75 W low pressure mercury lamp	0.75	Yao et al., 2023 [11]
Cylindrical 25 mL	18 W UV + 500 W Xe lamp	20.75	Yang Yu et al., 2017 [12]
Cylindrical 1100 mL	500 W UV-LED	0.45	Thammasak Rojviroon et al., 2013 [13]
Cylindrical 500 mL	1.7 W (total) *	0.0035	This study

* The power requirement of each lamp is 0.17 W and since ten lamps are used in the reactor, the total power requirement is 1.7 W.

2. Materials and Methods

2.1. Materials

Direct Blue 15 (DB15) dye was purchased from Sigma-Aldrich (Molecular formula: C34H24N6Na4O16S4, C. I. number 24400, M.W. 992.8 g mol^{-1}). Ultrapure water was used for preparation of the dye solutions and cleaning purposes. The used water was purified using a Milli-Q water system. P25 TiO_2 (Average particle: 30 nm, Surface area: 50 m^2 g^{-1}) was purchased from Degussa company, a composition of anatase 80% and rutile 20%. Figure 1 shows the chemical structure of DB15.

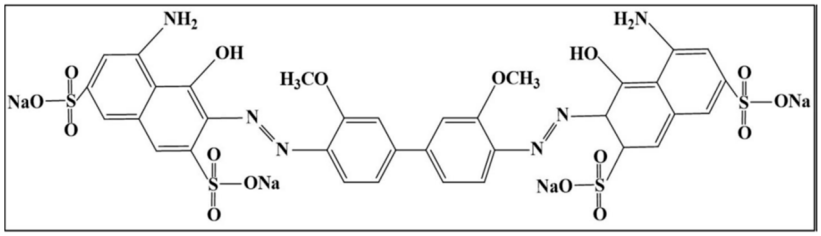

Figure 1. Chemical structure of Direct Blue 15 (DB15) [5].

Nitric acid (70%) and Potassium hydroxide provided by Sigma-Aldrich and Merck (Darmstadt, Germany), respectively for the purpose of pH adjustment. All chemicals were used without further treatment. Anhydrous sodium sulphate (Na_2SO_4) was obtained from Caledon Laboratory Chemicals. Methylene chloride (CH_2Cl_2: HPLC grade) was purchased from Macron Fine Chemicals and used as received without further purification.

2.2. Preparation of LED Light Bulbs

LED light bulbs were purchased from Hausprofi Bausysteme GmbH (ASIN B07TYZM67P). The light bulbs are waterproof and near spherical in shape, however it was found that there were openings around the bulb, where water could penetrate inside and reduce the lifetime of the lights. Therefore, all the openings were sealed using a waterproof glue (J.B. Weld (Water Weld)), which was in paste form and became hard when cured. Although these light bulbs are expected to float at the water surface and since their density is slightly

lower than that of water, they can be easily dragged into water and remain suspended by convective currents induced by stirrer inside the photoreactor. The density can also be adjusted easily by using lower or higher density sealants filling the voidage inside the bulb. Figure 2 shows the LED light dimensions and their use inside the photoreactor.

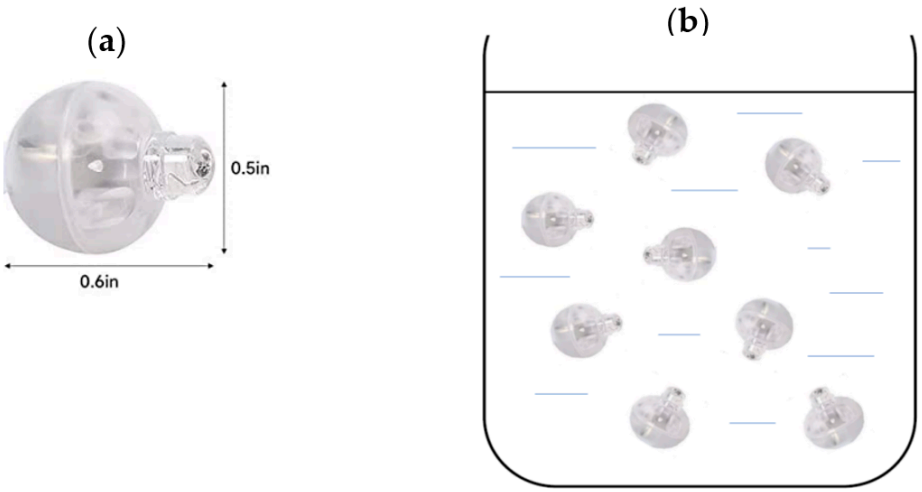

Figure 2. (**a**) Dimensions of the LED light bulb, (**b**) photoreactor with suspended lights.

The lights have a switch to be turned on before the experiments. These lights remain on for about 6 days, during which many experiments can be carried out. The used lights are discarded as they are too cheap to be regenerated and reused. Suspended lights with rechargeable batteries will be an option to be explored in near future to reuse the lights.

2.3. Experimental Setup

The experiments were carried out in a cylindrical reactor made of Pyrex with a volume of 1000 mL. The pH of the solution was adjusted at optimum value as described elsewhere [5].

In order to study the effects of the suspended light on deactivation of DB15, the operating conditions were kept similar to those of swirl reactor to have a common base for comparison. [5] The reactor was aerated with a continuous flow of air at 50 mL/min for about 30 min to become saturated with oxygen, after which the lights were introduced and degradation of DB15 started. A magnetic stirrer at 400 rpm was used to mix the reactor content and keep the light bulbs moving inside. The reactor and magnetic stirrer were held inside a sealed wooden box to eliminate interference of surrounding lights with the experiments; therefore, the only available light source was the suspended lights. Since the lights power was too small to change the temperature, negligible change in temperature was observed after 14 h of experiment and therefore no need for cooling. Figure 3 shows the experimental setup. Samples taken at 1–2 h time intervals. The samples were analyzed by a UV-Vis spectrophotometer (UV-3600, Shimadzu, Japan) and the spectrum was recorded within the range of 300–800 nm. The Total Organic Carbon (TOC) content of the samples was measured at different time intervals to find the extent of DB15 mineralization. The TOC measurements of the filtered samples were evaluated using a Shimadzu TOC-V CPN analyzer (Shimadzu, Japan). The TOC was measured at a temperature of 680 °C, which was high enough to oxidize all organic compounds.

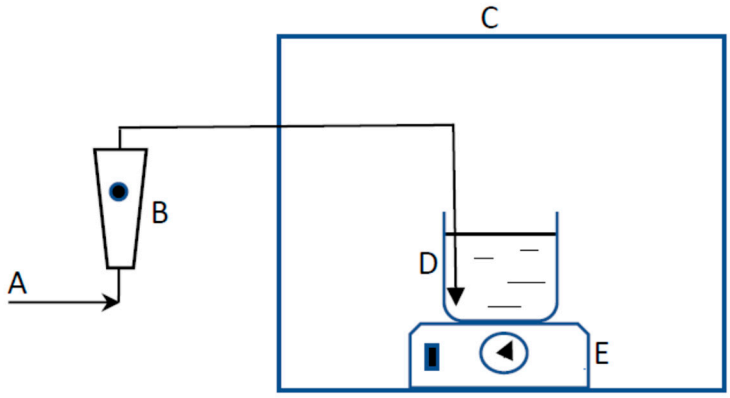

Figure 3. Schematic diagram of the batch reactor; (A) air supply, (B) Flow meter, (C) Wooden box (sealed), (D) Reactor, (E) Magnetic stirrer.

3. Results

Pure DB15 dye and demineralized water were used for preparation of samples. The absorption peak wavelength of DB15 was measured by the UV-Vis spectrophotometer at different concentrations to be used in analysis of samples as shown in Figure 4.

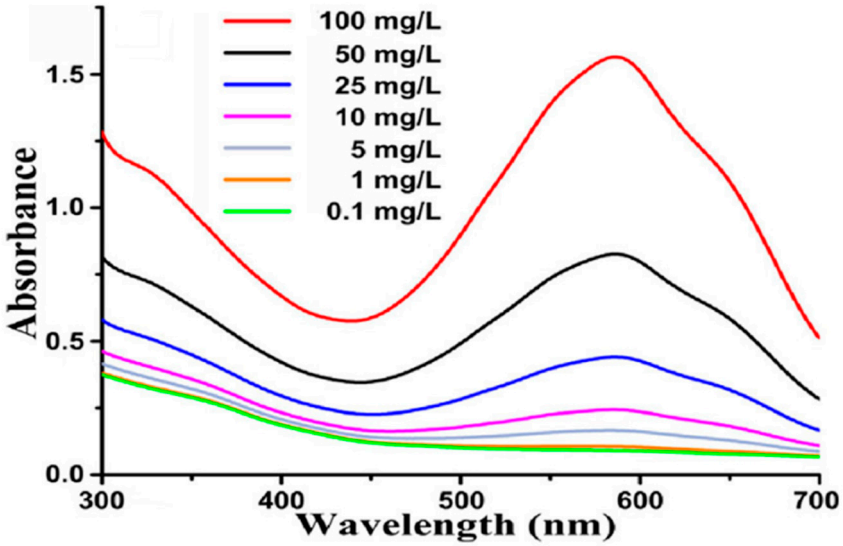

Figure 4. Absorption Peak wavelength of DB15 at different concentrations.

Experiments were carried out initial concentrations of 40, 18, and 14 mg/L and repeated three times (at least) to ensure reproducibility of the results, while catalyst concentration remained unchanged at 62.5 mg/L for all experiments. In the range of concentrations used the maximum absorbance was the wavelength of Bout 580 nm. These concentrations were selected due to availability of previously obtained data at identical conditions for comparison. Figure 5 shows degradation of DB15 with initial concentration of 40 mg/L.

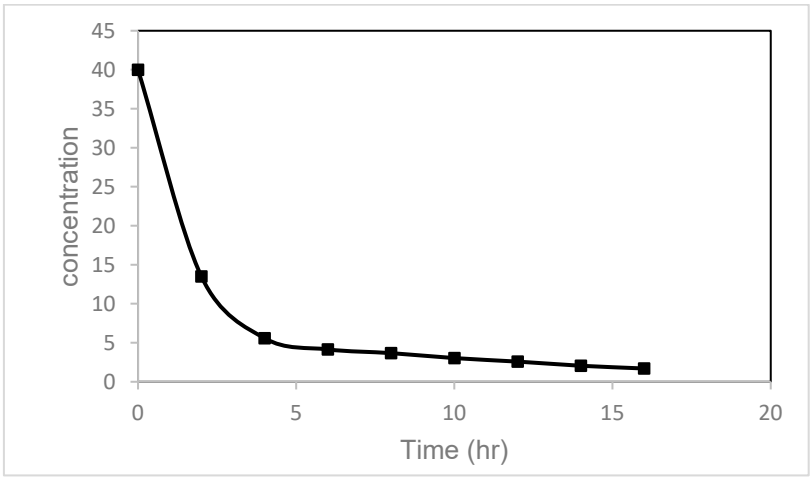

Figure 5. Degradation of DB15 dye at initial concentration of 40 mg/L. (standard deviation = 0.03).

The samples were also analyzed by UV-Vis spectrophotometer and similar trend was observed as shown in Figure 6.

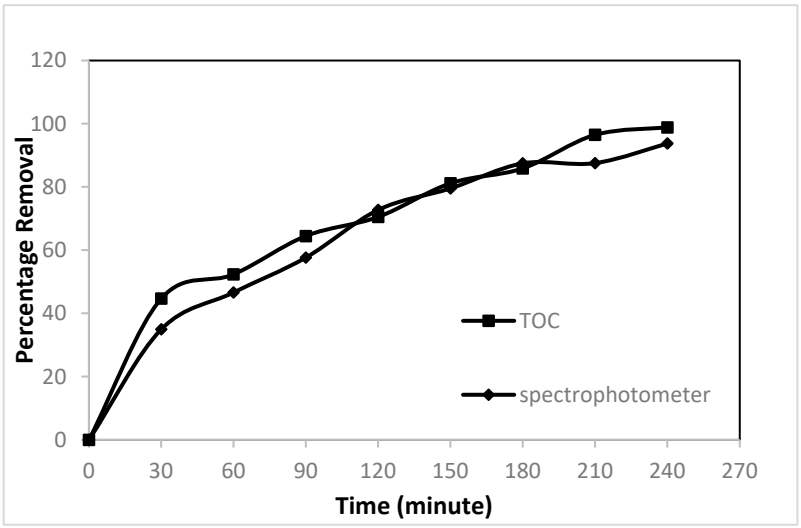

Figure 6. Degradation of DB15 at initial concentration of 18 mg/L. (Standard deviations, TOC = 0.036, UV-Vis. Spec. 0.02).

4. Discussion

Since there is no barrier (filter) or attenuation for light to reach the photocatalyst, we believe that small UV portion (~10%) of the visible light source will reach the photocatalyst surface and activate it as the reaction time was long and at nearly complete mixing achieved in the experiments, degradation occurred. Reflection of UV rays over the reactor wall may play a role in achieving higher efficiencies. The degradation was quite rapid in the first 4 h and decreased afterwards. In a similar experiment with UV light 75 reduction in concentration was observed in 14 h [5], while the same reduction was achieved in 7.5 h when suspended lights were used instead. The degradation time decreased by about 50% when suspended lights were employed. The results for lower concentrations are summarized in Table 2. The degradation rate was lower at low concentrations. At higher concentration photocatalytic degradation rate normally follows zero-order rate (independent of concentration) while at low concentration the rate is first-order (C vs. time plot is exponential decay). Since at low concentration the reaction rate is concentration dependent (reaction rate = kC), at low concentration degradation rate would decrease. Usually, photocatalytic

degradation rate follows Langmuir type rate expression [Rate = kKC/(1 + KC)], where k is reaction rate constant, and K is adsorption equilibrium constant. Above rate expression becomes zero-order at high concentration (KC >> 1) while at low concentration, rate becomes first-order (KC << 1). Obviously, the linear rapid mineralization occurs at high concentration, but it decreases as concentration decreases.

Table 2. The required degradation time for stationary and fixed lights.

Sample Initial Concentration mg/L	Degradation %	Time Requirements	
		This Study	Waleed et al. [5]
40	75	10 (h)	14 (h)
18	90	210 (min)	270 (min)
14	95	140 (min)	150 (min)

The limited lifetime of the suspended light (battery power limitation) is one of the challenges to be met in large scale operations. The use of rechargeable battery and in situ charging systems, which are proven technologies in commercial use can be explored and employed with minor modifications inside the reactor for large scale operations. It is out of the scope of this study now, subject to future investigation.

5. Conclusions

Suspended LED lights were used to study degradation of DB15 dye. It was found the degradation rate was higher compared to stationary UV light (proof of concept). The degradation rate almost doubled when suspended lights used inside the reactor, and therefore the reactor size would be smaller due to the decrease in residence time, leading to lower reactor cost. The difference in degradation rate was more profound at higher initial concentrations due to independency of rate on concentration. At lower initial concentration the degradation rate decreased as the rate becomes concentration dependent following first order kinetics. Further studies are required to meet the challenges related to operations in large scales such as using rechargeable batteries and in situ recharging system.

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