APPLICATION OF HIGH POWER UV LEDs IN HETEROGENEOUS PHOTOCATALYSIS

Máté Náfrádi, Tamás Hlogyik, Luca Farkas, Tünde Alapi

Department of Inorganic and Analytical Chemistry, University of Szeged, H-6720 Szeged, Dóm tér 7, Hungary
e-mail: nafradim@chem.u-szeged.hu

Abstract

In our work, we designed and built a photochemical reactor with High Power LED light sources, and then tested its operation by heterogeneous photocatalytic decomposition of coumarin. The UV-LEDs emitting at a wavelength of 367(±10) nm were built into a frame with air-cooling elements. A well-controlled electrical power source was used to control and regulate the light output of the LEDs. The photon flux was measured at different electric power inputs, and was found to be linearly dependent on electrical power. Coumarin was used to test the new photoreactor during heterogeneous photocatalysis using TiO_2 and ZnO as photocatalysts. At low photon flux the UV-LEDs outperformed a fluorescent mercury-vapor lamp in terms of efficiency and power consumption, but their usage at high electric input is not favorable.

Introduction

Advanced Oxidation Processes (AOPs) are a possible solution to some emerging environmental problem, such as the elimination of organic pollutants from waters. Several AOPs include the use of UV light, like O_3/UV, UV/Cl_2, photo-Fenton reactions, or heterogeneous photocatalysis. Generally the used light sources are mercury-vapor lamps, but these have some drawbacks, like fragility and hazardous waste production. In the last few years, with the advances in optoelectronics the application of Light Emitting Diodes (LEDs) emitting in the UV region gained more and more popularity. With the application of High Power LEDs the mercury vapor lamps emitting in the 300-400 nm region can be replaced with other UV light sources. UV-LEDs emitting in the UV-C region (260-290 nm) are already available, but their power-efficiency is still relatively low (1-5 %). Due to the further improvements they might also provide a good alternative for mercury vapor lamps emitting UV-C photons (254 nm) [1,2].

UV LEDs that emit at 300-400 nm are especially useful for heterogeneous photocatalysis, since the most frequently used catalysts, TiO_2 and ZnO can be excited with light having wavelength shorter than 390 nm. Due to the absorption of photons having appropriate energy (~3.2 eV), excited conduction band electrons (e_{cb}^-) and valence band holes (h_{vb}^+) form, and they initiate the transformation of organic compounds via charge transfer or hydroxyl radicals (HO•) based reactions. UV-LEDs have already been used in the last few years with good efficiency to transform various pollutants in aqueous media [3-5].

The goal of this current study was to plan, and build a new photoreactor equipped with high power UV-LEDs, and test it for use in the field of heterogeneous photocatalysis. The effect of electric input, and the distance between the reactor wall and light sources were investigated. The photon flux absorbed by the treated solution was determined with actinometry. To test the light sources during heterogeneous photocatalysis, TiO_2 and ZnO as photocatalysts, and coumarin (COU) as a model compound were used. The formation of the hydroxylated product of COU, 7-hydroxy-coumarin (7-HO-COU) allows the estimation of HO• formation rates [6].

Experimental

The Vishay (VLMU3510-365-130) high power UV-LEDs emitting at 367 nm wavelength were supplied by Distrelec Hungary. The LEDs use InGaN die, and are equipped with a high purity silicone lens. Their typical opening voltage is 4.0 V, and they have a radiant power of 690 mW (with a typical 2000 mW power consumption). They have been soldered to star shaped metal core printed circuit boards (MCPCB) supplied by Meodex. Due to the high amount of heat generated by the LEDs, 0.70 K/W aluminum heat sinks were used to convey the heat. An AX-3005DBL-3 laboratory power supply (maximum output is 5.0 A / 30.0 V) was used to provide and precisely control the electrical power needed to operate the light sources. The irradiated solution was held in a 200 cm^3 cylindrical glass reactor that can be bubbled with gas from a porous glass filter at the bottom. Depending on the measurements, N_2 (99.995 %) or synthetic air was used.

The photon flux of the light sources were measured using ferrioxalate actinometry, as described by Hatchard and Parker [7]. 1.0×10^{-2} M Fe(III)-Oxalate solutions were irradiated, the released Fe(II) was measured using 0.2 % phenanthroline. The absorbance of Fe(II)-phenanthroline complex was measured at 510 nm using UV-Vis spectrophotometry (Agilent 8453) in a quartz cuvette with 0.20 cm optical path length. The solutions were bubbled during the measurements with N_2 (99.995 % purity).

The photocatalytic measurements were performed in the previously described UV-LED system, or in a 500 cm^3 glass reactor irradiated using a 15 W mercury vapor lamp emitting between 300-400 nm (GCL303T5/UVA, LightTech) as a reference. Before the measurements, the suspensions were saturated with synthetic air, and they were stirred in the dark for 30 minutes. The samples taken were centrifuged at 15000 RPM, and filtered through a 0.22 µm syringe filter. The experiments were started with turning on the light sources. During the photocatalytic experiments suspensions of TiO_2 (Aeroxide P25) and ZnO (Sigma Aldrich) were irradiated. COU concentration was 5.0×10^{-4} M, its concentration was determined via UV-Vis spectrophotometry at 277 nm. The formation of 7-HO-COU was measured using fluorescence spectroscopy (Hitachi F-4500), the excitation wavelength was 345 nm, while the detection was performed at 455 nm wavelength. Reaction rates were determined from the initial linear part of the kinetic curves (up to 15 % transformation of COU).

Results and discussion

As the first part of the current work, the new LED reactor was planned, and built. The 12 pieces of UV-LEDs were soldered according to their manual to the MCPCB stars. Two LEDs were fastened to each heat sinks, the adequate heat conductivity was provided by thermal paste. The two LEDs on one heat sink was connected in series, and the six parts were connected in parallel, resulting in 8.0 V maximum applicable voltage and 3.0 A maximum applicable current. The six heat sinks are fastened to an aluminum base, their distance from the glass reactor can be changed from 1.25 to 4.25 cm (Fig. 1).

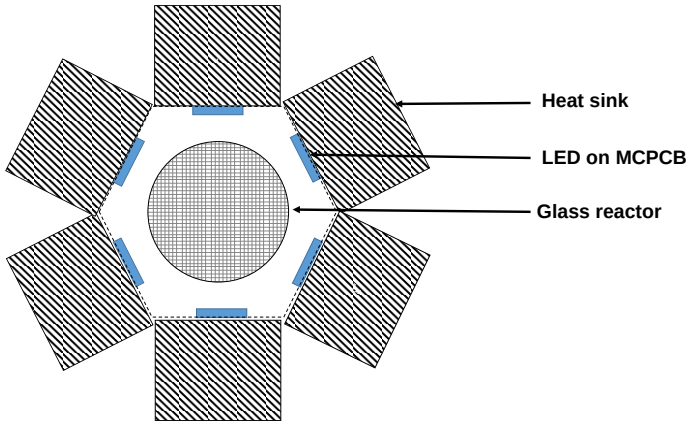

Figure 1. Schematic setup of the reactor (top view), with the LEDs

The reactor was tested using ferrioxalate actinometry to determine the photon flux, and compare it to the mercury vapor lamp. The measurements were performed with different electrical parameters, from 3.39 to 20.77 W. The voltages were set to constant 8.0 V (6.8(±0.1) V measured when turned on), and the current was changed from 0.5 to 3.0 A. The absorbance of the Fe(II)-phenanthroline complex was measured at 510 nm according to literature [7], and the photon flux was calculated from the slope of the line fitted (Figure 2/A). The light emission of UV-LEDs showed very good linearity as a function of electrical energy consumption. The photon flux of the mercury-vapor lamp was also determined (Figure 2/B), and we can see the much greater efficiency of the LED light sources, as they provide ~60 % more photons at similar electric power consumption.

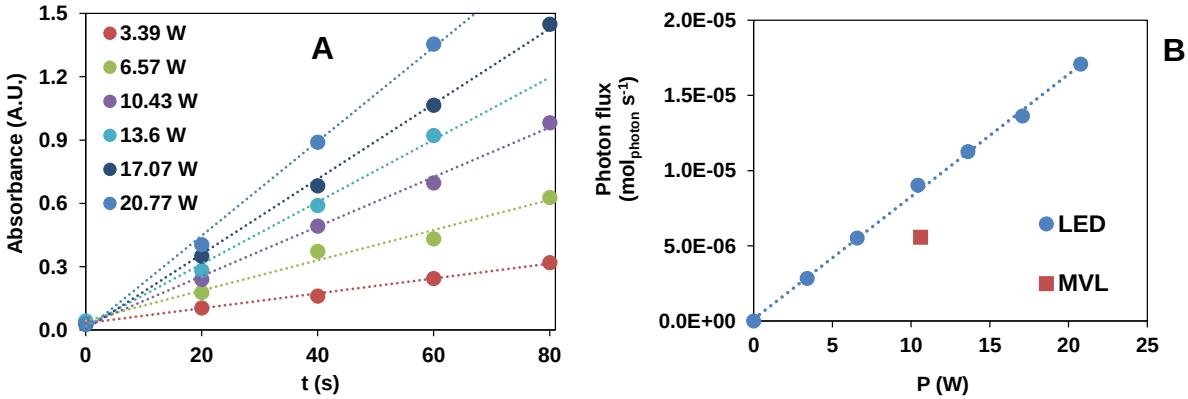

Figure 2. The absorbance values measured at 510 nm as a function of irradiation time at different electric power output (A), and the calculated photon flux of the LEDs compared with the Hg-vapor lamp (B)

The effect of the distance (r) between the LEDs and the glass reactor on the photon flux was also determined at constant power input (13.6 W). The photon flux was reduced with the distance from the light source. Therefore the best option is to use the light sources at the closest position (r = 1.25 cm). The possibility to irradiate a larger volume via changing the distance and using a reactor having a larger diameter is an advantage of this reactor setup.

The LED reactor was tested using TiO_2 P25 Aeroxide and ZnO photocatalysts and COU, as model compound. The hydroxylated product of COU, 7-HO-COU only form during reactions with HO•, therefore it can be used to determine the formation rate of HO• [6]. First, the optimal catalyst concentration was determined, since it greatly depends on the reactor size and design, and light intensity. 5.0×10^{-4} M solutions of COU was irradiated in the presence of

TiO_2 and ZnO. The LEDs were operated at 13.6 W (photon flux = 5.63×10^{-5} mol_{photon} sec^{-1} dm^{-3}). The reaction rate of COU did not change above 0.5 g dm^{-3} catalyst load (Fig. 3/A), similarly to the formation rates of 7-HO-COU, it even started to lower at high (1.5 g dm^{-3}) ZnO dosage (Fig. 3/B), probably because of the increased light scattering. During further experiments, 1.0 g dm-3 catalyst concentration was used, to exclude the contribution of direct photolysis.

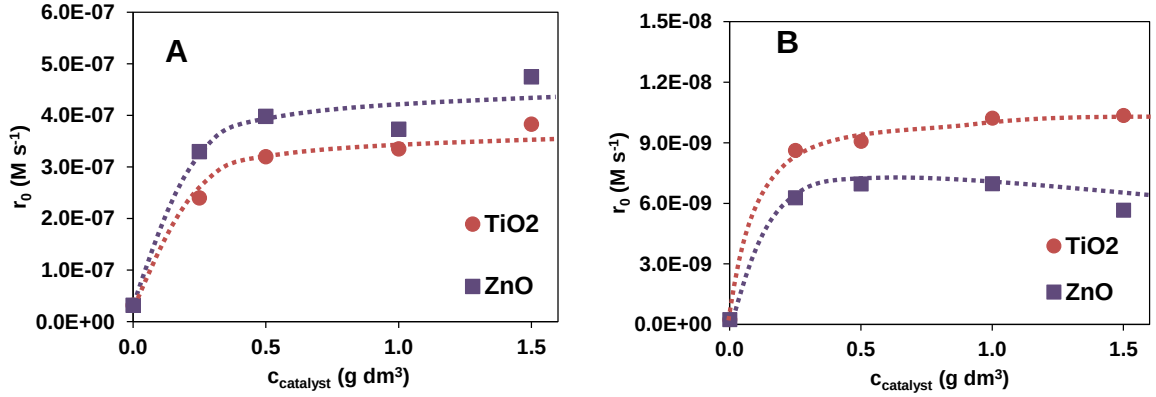

Figure 3. The transformation rate of COU (A), and the formation rate of 7-HO-COU (B) as a function of catalyst concentration

The reaction rates of COU, and the formation rates of 7-HO-COU were determined at different photon fluxes by varying the electric power input (3.07 - 21.14 W) of the LEDs. Although the photon flux increased linearly with electric power input, in the presence of catalysts the reaction rates of COU increased according to a saturation curve (Fig. 4/A). The formation rate of HO• showed a similar tendency (Fig. 4/B). The apparent photonic efficiencies can be calculated using the photon flux determined via actinometry. With the increase of the photon flux the photonic efficiency of the transformation of COU reduced from 1.5 % to 0.5 %.

In the case of measurements with the Hg-vapor lamp similar photonic efficiencies were measured (1.1 %). The results have been corrected according to the different reactor volumes. If we take these into account then the difference is negligible, therefore the cost-efficiency of the two light sources is similar (Fig. 4).

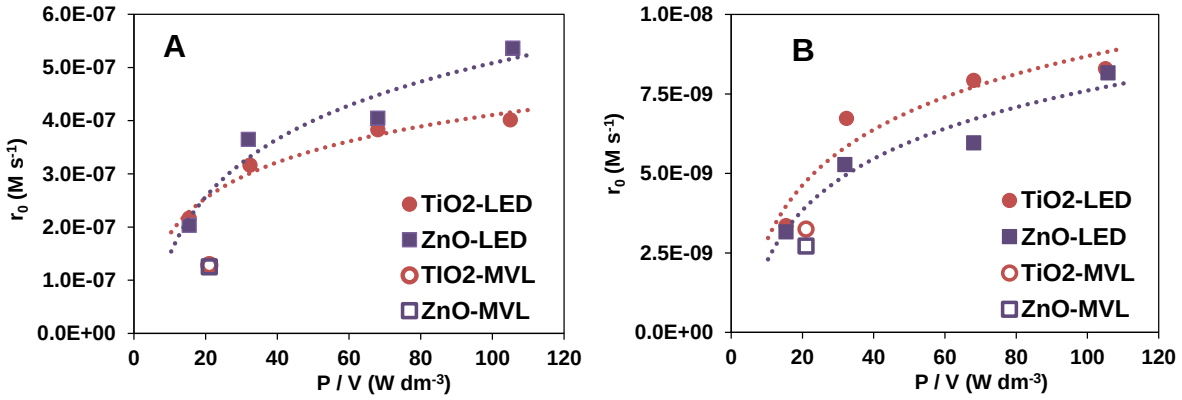

Figure 4. The transformation rate of COU (A), and the formation rate of 7-HO-COU (B) in the case of LEDs and Hg-vapor lamp as a function of electrical power used

Conclusions

The constructed high power UV-LED based photoreactor setup was highly efficient, and well customizable for use with either photolytic of photocatalytic applications. Overall, we can conclude, that the use of LED light sources for photochemical applications is highly favorable

due to their power efficiency, and customizability. The operation of the LEDs is especially cost-effective in the case of lower electric energy input.

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