Photoinduced Advanced Processes in Times of Minamata Convention on Mercury: Perspectives and Challenges

ORAL
Ph.D. Student: N
Journal: ESPR

E. Fagnani[1], *N.C.Silva*[1], *F.Banhi*[2]. *(1) Universidade Estadual de Campinas - School of Technology, Rua Paschoal Marmo 1888, Limeira SP 13484-332, Brazil, enelton@ft.unicamp.br. (2) VeRSis Technology Ltda, Rua Monte Aprazível 216, Campinas SP 13090-764, Brazil.*

Since 2013, formal efforts of many countries have been dispensed towards the banishment of mercury from the industrial processes, culminating in the Minamata Convention on Mercury - MCM (2017), a environmental program from United Nations, which is signed by 148 parties nowadays, including Brazil. Adopting the MCM includes, among other things, the cessation of manufacturing, importing and exporting mercury-based lamps, which is a problem for researchers and companies that rely on ultraviolet light photo-induced advanced processes for effluent treatments. This work discusses the use of light emission diodes (LEDs) for the replacement of mercury-based lamps regarding environmental issues, quantum yields, and design of the reactors. Results showed, under the experimental conditions, the UV-LEDs used in the study were unable to promote photolysis, able to promote photoperoxidation (advanced oxidation process) and barely able to promote photosulphitization (advanced reduction process). The importance of the disposition of diodes into the illumination system is also discussed.

Introduction

Photoinduced Advanced Oxidation Process (photo-AOP) is a technology effectively used in wastewater treatment aiming to water reuse worldwide, in order to mitigate the serious problem of global drought caused by climate change crisis [1]. Normally, photo-AOPs are combined with other techniques in a multibarrier-type wastewater treatment, as can be seen in Orange County CA, EUA [2]. More recently, photocatalyzed Advanced Reduction Processes (photo-ARPs) have been employed as emergent technologies that promise the reductive degradation of more oxidized compounds as poly/perfluorinated substances, nitrate, perchlorate and others [3,4]. Both photo-AOPs and photo-ARPs rely on ultraviolet radiation, normally type C (200 - 280 nm spectral band), provided by low pressure mercury-based lamps (LP-UV), which present an intense and characteristic emission in 254 nm capable to generate radicals and to promote disinfection at some level. International pressure for ceasing extraction and use of the mercury in the anthroposphere has been done over the years and it has been intensified since 2017 with the Minamata Convention on Mercury (MCM) from the United Nations [5]. Such global treaty provides to ban mercury-based products and associated processes, which inescapably encompasses the ordinary UV lamps. Some alternative UVC light sources have been studied, with highlight to excimer lamps (170 - 230 nm), and the chip-scale devices as the cathodoluminescent (CL) (260 - 265 nm) and the light emitting diodes (LEDs, ≈ 265 nm) [6]. The present work compares the traditional LP-UV Hg-based lamps to UV-LEDs concerning the efficiency and design of illumination systems, in order to promote the processes of photolysis, photoperoxidation (a photo-AOP) and photosulphitization (a photo-ARP).

Material and Methods

A cylindrical reactor constituted of quartz (450 mL) was used for the batch experiments. Three different LED illumination systems, which were situated at the outside of the body quartz (figures 1 and 2) were alternately tested.

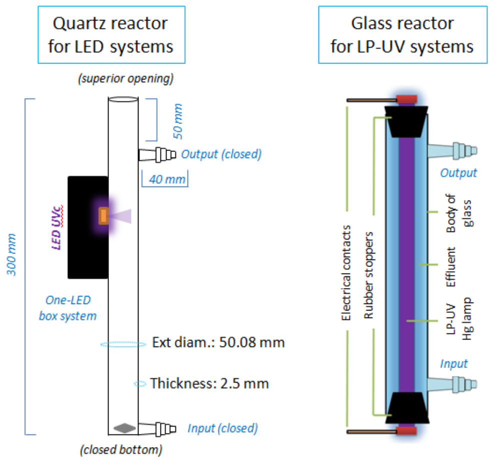

Figure 1. Reactors for LED-based lighting systems (left) and for LP-UV Hg-based lighting systems (right)

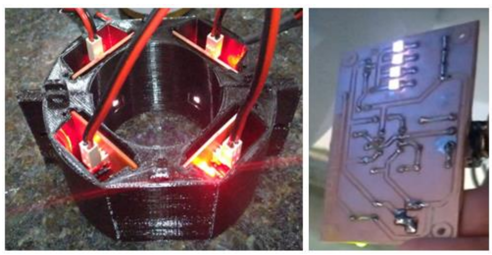

Figure 2. Design of lighting systems: Handcuff system (left) and the inner circuit of a four-LED Box system (right). Both Box and Handcuff systems were constructed with polylactic acid (PLA) from a 3D-printer.

The LEDs were based on aluminum gallium nitride with maximum emission at 273 nm and rated power of 15 mW. For comparison purposes, the experiments were also conducted in a glass cylindrical reactor containing a LP-UV tubular Hg-based lamp (254 nm) internally placed at the center [7], which had a rated power of 15 W (one thousand times higher than the LED). The three LED systems were defined as: (a) one-diode in box system, (b) four-diodes aligned in box system, vertically arranged (distance lesser than 1 mm among them), and (c) the handcuff system, with 4 diodes horizontally disposed under a crossed arrangement (Figure 2). Chemical actinometry using ferrioxalate [8] was used to compare the quantum yield among the box systems and LP-UV system. Additionally, the monitoring of methylene blue (MB) photodegradation, a recognized compound used for assessing AOPs systems [6,7,9], was employed to evaluate the efficiency of the LED systems. Moreover, the influence of the arrangement of diodes in the systems four-LED in box (next and lined up) and four-LED in handcuff (at 90 degrees in a crossed plan) was investigated. Finally, it was tested the efficiency of the four-LEDs in box system in comparison with the LP-UV system for the photocatalytic reduction of nitrate with sulphite (photosulphitization, ARP). All the tests were monitored through spectrophotometric analysis, taking aliquots every 15 min for 2 h of experimentation at least.

Results and Discussion

Despite the remarkable difference between the rated power of the LP-UV lamp and the UV-LED (1,000 times), it was possible to see chemical transformations yielded by the reactor with LED even from only one diode. The actinometry showed no significant difference in quantum yield from the comparison between the two box systems, with one LED and with side by side four LEDs. The same magnitude order (10^{17}) of photons per second was obtained in both box systems, suggesting that the use of four LEDs or only one LED provides the same efficiency, which were lesser than the obtained in the LP-UV system (10^{18}). The difference between the maximum emission bands of the two light sources (LP-UV and LED) is other very important issue: UV LEDs (λ_{max} 265 nm) were not able to photolyze MB (Figure 3), in opposition to the LP-UV lamp (λ_{max} 254 nm) [7,9].

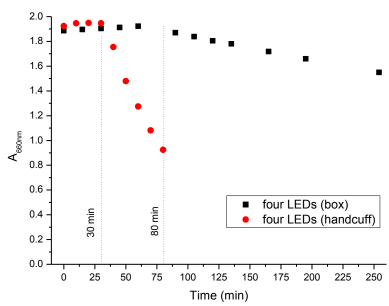

Figure 3. Kinetic degradation of methylene blue through photolysis (first 30 min) and photoperoxidation (from 30 min onwards) by (■) four-LED in Box system and (●) four-LED in Handcuff system

However, LED systems were able to degrade MB in the presence of hydrogen peroxide (photoperoxidation, AOP) like with LP-UV lamps. The spatial arrangement of the LEDs in the systems was crucial in the efficiency, as suggested in the literature [10]. MB was degraded by both LED systems: four-LED Box system and four-LED Handcuff system. However, the kinetics was favored when the handcuff system was employed (Figure 3). This result disagrees with the chemical actinometry, because it was used the four-LED in Box system (aligned and next LEDs) rather than the Handcuff system (farther LEDs in a crossed disposition). This result suggests that the arrangement influences the efficiency of the reactor. Additionally, it was tested the reduction of nitrate with sulphite under UV light (ARP). Nitrate was efficiently reduced in LP-UV system, but only slightly by the four-LED handcuff system (Figure 4).

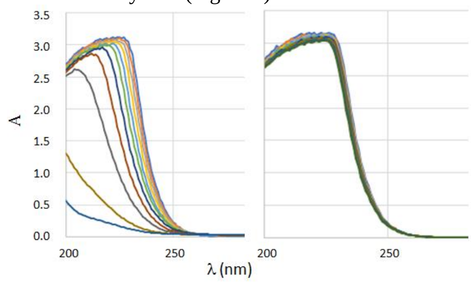

Figure 4. Nitrate degradation by UV-$SO_3^{\bullet-}$ (ARP) using LP-UV lamp (left) and LED handcuff system (right).

Conclusions

UV-LED is a potential source for the replacement of LP-UV lamps in photo-AOPs. Main advantages are low energy consumption, long lifespan, mercury-free and chip-scale technology. Photolysis and ARPs were not effectively achieved with UV-LEDs. The arrangement of the diodes is crucial for the efficiency of degradation.

Acknowledgments

Authors thank to CNPq for the scholarship of N.C.Silva.

References

[1]E. Savelli, M. Rusca, H. Cloke, G. Di Baldassarre, *WIREs Climate Change*, (2022) 13:e761. DOI: 10.1002/wcc.761

[2]P. Jeffrey, Z. Yang, S.J. Judd, *Water Research*, 214 (2022) 118198. DOI: 10.1016/j.watres.2022.118198

[3]B.P. Vellanki, B. Batchelor, A. Abdel-Wahab, *Environmental Engineering Science*, 30 (2013) 264. DOI:10.1089/ees2012.0273

[4]Y.Cao, W.Qiu, J. Li, J. Jiang, S. Pang, *Science of the Total Environment*, 765 (2021) 142762. DOI:10.1016/j.scitotenv.2020.142762

[5] *Minamata Convention on Mercury: text and annexes*, UNEP Chemicals, Nairobi, UNEP, 2013.

[6]V.K. Sharma, H.V. Demir, *ACS Photonics*, 9 (2022) 1513. DOI: 10.1021/acsphotonics.2c00041

[7]E. Fagnani, R.A. Guadagnini, G.A. Silva, J.R. Guimarães, *HOLOS Environment*, 13 (2013) 85. DOI: 10.14295/holos.v13i1.5775

[8]S. Goldstein, J. Rabani, *Journal of Photochemistry and Photobiology A: Chemistry*, 193 (2008) 50. DOI: 10.1016/j.jphotochem.2007.06.006

[9]J.A. Malvestiti, E. Fagnani, D. Simão, R.F. Dantas, *Environmental Technology*, 40:15 (2019) 1910. DOI: 10.1080/09593330.2018.1432698

[10]B. Jasenak, *IUVA News*, 20 (2018) 10