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Investigation of variables affecting UV-LED photocatalytic degradation of antibiotics ciprofloxacin and sulfamethoxazole

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Abstract

In this study, photolytic and photocatalytic degradation of two antibiotics in ultra-pure water were analyzed. A lab-scale cylindrical reactor had its inner walls impregnated with TiO_2 nanofilm for the photocatalytic experiments. In the first step, an optimized photoreactor design was chosen based on the degradation of ciprofloxacin (CIP) under UV-A. The impact of controlled periodic illumination (CPI) on kinetic rates and energy expenses was also studied. In the second step, degradation of both ciprofloxacin and sulfamethoxazole (SMX) were analyzed at different wavelengths (UV-A and UV-C) using the photoreactor design selected in the first step. Results show the optimization benefits of an appropriate photoreactor and CPI for photocatalysis. Each compound's reactivity to different degradation pathways plays a major role in the process, so a careful study of the particularities of each system is paramount for lowering energy expenses.

Keywords: Ciprofloxacin; Light-emitting diodes; Photocatalysis; Photoreactor design; Sulfamethoxazole; Ultra-violet

1. Introduction

The development of light-emitting diodes (LEDs) able to produce UV light opens up many possibilities for water treatment[1]. Innovative photoreactor designs, controlled periodic illumination (CPI) and specifically-tailored wavelength emission are among the new tools engineers have to reduce energy expenses of photocatalysis, which still rank high even among other advanced oxidation processes (AOPs) due to its low photonic efficiency[2]. A well-accepted way to evaluate the performance of different AOPs is to compare their electrical energy consumption (E_{EO}), defined as the required energy to degrade 90% of a pollutant in 1 m^3 of treated volume[2]. Photocatalysis generates highly oxidative radicals able to degrade recalcitrant compounds of emerging concern, such as antibiotics. Their presence in water can increase bacterial resistance, which continuously presses the development of new and stronger pharmaceuticals[3].

Considering the significant number of variables which influence photocatalytic processes, this study proposes to evaluate degradation of two antibiotics under different circumstances to further understand this process and contribute finding optimization possibilities.

2. Materials and Methods

Two cylindrical photoreactors made of quartz were used (r = 1.85 cm, L= 15 cm and wall thickness = 1.5 mm), one of them impregnated with TiO_2 nanofilm. Initial reaction volume was 150 mL. The reactor was illuminated by UV-LED strips of different wavelengths (254 and 365 nm)[4,5] glued on a cylindrical structure positioned around the reactor, illuminating it from the side. It was possible to turn on 3 or 6 (radially symmetric distributed) strips simultaneously and vary their distance from the reactor's walls (10 and 15 mm). To vary the LED's duty cycle (DCy) during controlled periodic illumination (CPI) experiments, an ARDUINO microcontroller was added and programed with pulse-width modulation function (Heaviside step). Photodegradation experiments ran for one hour (total illumination time). Samples were collected at regular intervals and then residual concentrations of ciprofloxacin (CIP) and sulfamethoxazole (SMX) were analyzed by chromatography (HPLC-DAD). A fan was kept on to avoid LED overheating and constant reaction temperature of 20 °C. CIP and SMX solutions were prepared using high-purity analytical standards and ultra-pure water. Initial concentration (C_0) of CIP solution in the first set of experiments was 10 mg/L, while both CIP and SMX in the second step were 2 mg/L. In the first set of experiments, different LED arrays and DCy were used to study degradation of CIP using UVA-LED. In the second set of experiments, LED strips with different wavelengths were tested to study the degradation of both compounds using the photoreactor design selected on the first step.

3. Results and Discussion

3.1 Degradation of CIP via UV-A

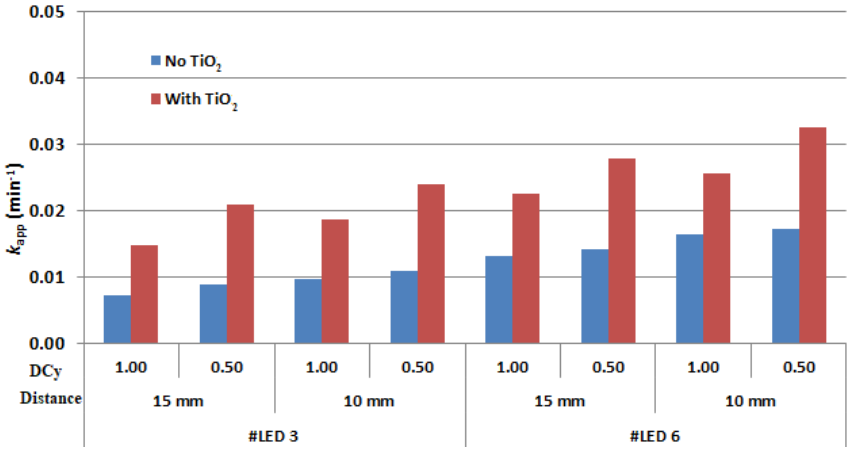

Figure 1: Apparent degradation rates of CIP under different scenarios for the 1st step

Figures 1 and 2 show the apparent 1st order kinetic constant rates k_{app} (min^{-1}) and E_{EO} values (kWh m^{-3}), respectively, for CIP degradation in the first step. All tests performed with the TiO_2 nanofilm had faster degradation than the ones without. This demonstrates the impact of radical formation for opening new and faster reaction routes for CIP when compared with UV-A photolysis alone. By looking at fig. 1, adoption of more light sources and shorter distances also increased CIP

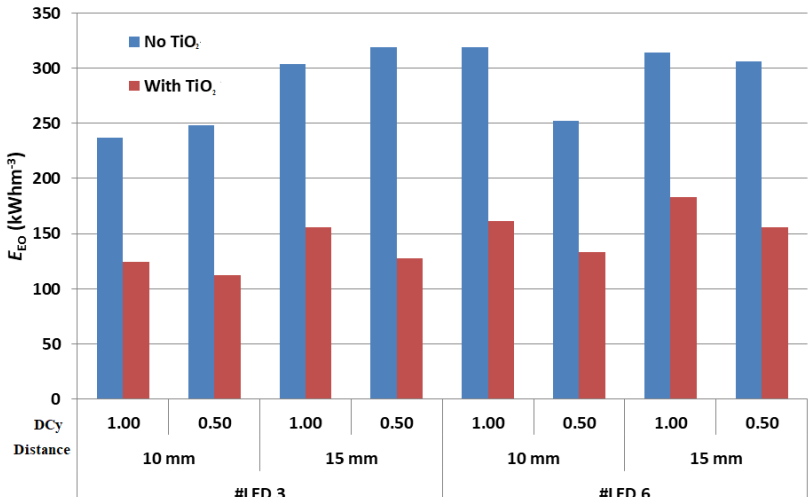

Figure 2. E_{EO} values for CIP degradation under different scenarios for the 1st step

reaction rate. However, by analysing **fig. 2** it can be verified that, when performed under the same circumstances, experiments using more LED sources had higher energy demands. This highlights the importance of an appropriate photoreactor design. Being so, the selected design for the 1st step was with 3 LED columns (distance 10 mm). Concerning CPI, the beneficial effects of lower duty cycles were only verified during experiments containing the TiO_2 nanofilm, which illustrates that radical-based reactions can happen under dark while photolytic-based reactions cannot[6].

3.2 Degradation of CIP and SMX via UV-A and UV-C

Figures 3 and 4 show the apparent 1st order kinetic constant rates (min^{-1}) and E_{EO} values (kWh m^{-3}), respectively, for CIP and SMX degradation in the second step. When comparing CIP degradation under different

C_0s (1st vs 2nd steps), rates with and without catalyst were slightly higher for the 2 mg/L concentration, since additional molecules reduce the availability of radicals and photons for photocatalytic and photolytic reaction routes, respectively, for the target compound6. It is evident by **fig. 3** that each substance reacts very differently towards each method. Unlike CIP, SMX is impervious to UV-A photolysis. Additionally, SMX is more reactive towards UV-C photolysis than CIP. SMX degradation by UV-C photolysis is so fast that the presence of TiO_2 hindered the apparent reaction rate and increased energy expenses (**fig. 4**). A possibility is that the nanofilm creates a screening effect, given that UV-C light has lower penetration capacities than UV-A. For SMX, the increase in degradation provided by the generation of radicals does not compensate for the losses in available photons for photolytic degradation using UV-C. Comparing degradation by UV-A photocatalysis, it can be inferred that SMX reacts slower with radicals species than CIP does, given that the degradation's increase compared with their respective UV-A photolysis values is lower for SMX than CIP **(fig. 3**). Although CIP has faster photolytic degradation by UV-C than UV-A, in the presence of the catalyst UV-A had the faster degradation, again demonstrating the considerable UV-C screening effect caused by the TiO_2 nanofilm, potentially hindering the process. **Fig. 4** shows that photocatalytic degradation under UV-A had the lowest energy consumption for CIP, since it takes advantage of the

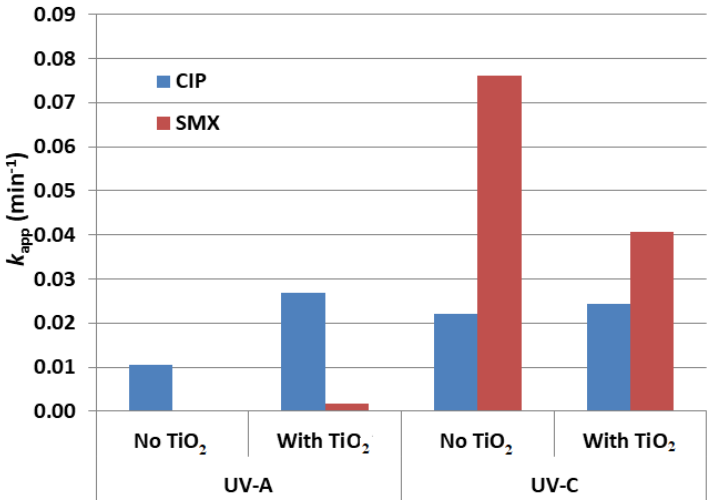

Figure 3. Apparent degradation rates of CIP and SMX under different scenarios for the 2nd step

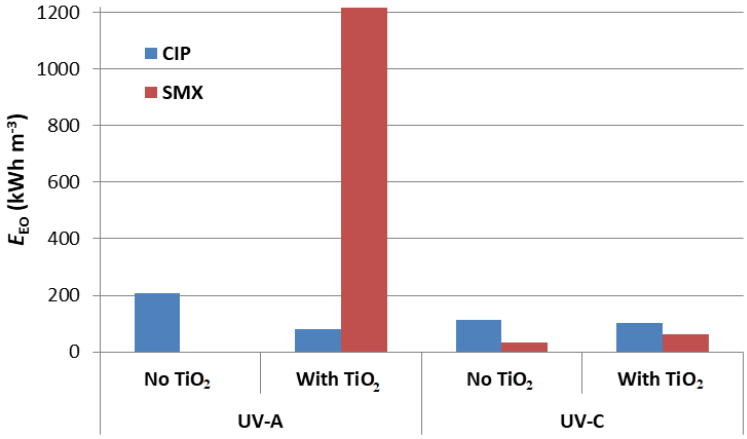

Figure 4. E_{EO} values for CIP and SMX degradation under different scenarios for the 2nd step UV-A for SMX without catalyst not shown (infinite value)

reactivity of this compound by both photolysis and radical species, with lower TiO_2 screening effects from UV-A when compared to UV-C.

4. Conclusions

Each target compound has different reactivity towards the multiple possible reaction pathways which can take place during photocatalysis, and their particularities must be understood for an efficient degradation. This work contributes to further understanding of UV-LED photocatalytic processes for antibiotic degradation and demonstrates that a large number of variables can have a significant impact on this technology, which is still at its early stages. More experiments evaluating degradation of a variety of pollutants of emerging concern under real treatment conditions (e.g. different matrices, lower initial concentrations) exploring the new design possibilities given by UV-LED are urgent for more sustainable water treatment processes.

5. Acknowledgements

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References

1. Chen J., Loeb S., Kim J. (2017) LED revolution: Fundamentals and prospects for UV disinfection applications. Environmental Science: *Water Research and Technology* **3**, 188–202.

2. Miklos D., Remy C., Jekel M., Linden K., Drewes J., Hübner U. (2018) Evaluation of advanced oxidation processes for water and wastewater treatment – A critical review. *Water Research* **139**, 118–131.

3. Sabri, N. Schmitt, H., Van der Zaan, B., Gerritsen, H., Zuidema, T., Rijnaarts, H., Langenhoff, A. 2018 Prevalence of antibiotics and antibiotic resistance genes in a wastewater effluent-receiving river in the Netherlands. *Journal of Environmental Chemical Engineering* **8**.

4. Waveform Lighting. RealUV LED Strip. Available at: https://store.waveformlighting.com/collections/led-strips/products/real-uv-led-strip-lights?variant=12527605252198. (Acessed: 27th November 2020)

5. Waveform Lighting. Clean UV-C Flex Strips Datasheet. Available at: https://www.waveformlighting.com/datasheets/CS_7026.pdf. (Accessed: 27th November 2020)

6. Bertagna Silva D., Buttiglieri G., Babić S. (2020) State-of-the-art and current challenges for TiO_2/UV-LED photocatalytic degradation of emerging organic micropollutants. *Environmental Science and Pollution Research* **28**, *1-8*