Photodegradation of CECs in Urban Wastewater: Comparative Study of Light-Driven AOPs in a FluHelik Photoreactor

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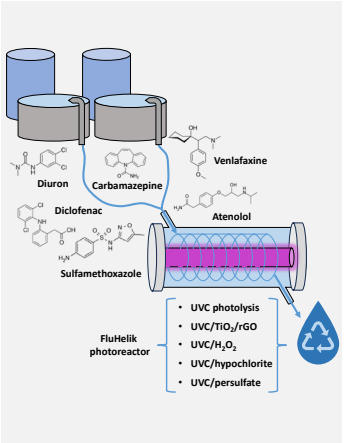

This study investigates the performance of different light-driven advanced oxidation processes (AOPs), using a tubular photoreactor, FluHelik, for degrading six target contaminants of emerging concern (CECs) commonly found in secondary treated urban wastewater. CECs include the pharmaceuticals atenolol (ATNL), carbamazepine (CBZ), diclofenac (DCF), sulfamethoxazole (SMX), venlafaxine (VLX), and the herbicide diuron (DRN). Results indicate that UVC photolysis effectively removes DCF, SMX, and DRN, while photocatalysis with titanium dioxide-reduced graphene oxide (TiO_2/rGO) requires further optimisation. The addition of oxidants - hydrogen peroxide (H_2O_2), hypochlorite ($HOCl/OCl^-$) and persulfate (PS, $S_2O_8^{2-}$) - significantly enhances the removal of CECs, with UVC/H_2O_2 and UVC/PS processes being the most effective. These findings contribute to the development of tailored treatment strategies for mitigating the presence of CECs in urban wastewater.

Introduction

Upgrading urban wastewater treatment plants (WWTPs) to remove contaminants of emerging concern (CECs) is becoming essential due to upcoming severe regulations on the discharge of these compounds to the environment [1]. Advanced oxidation processes (AOPs), particularly light-driven AOPs, offer solutions to complement conventional treatments in WWTPs. Within these processes, photocatalysis using titanium dioxide with reduced graphene oxide (TiO_2/rGO), and photochemical oxidation with various oxidants - hydrogen peroxide (H_2O_2), hypochlorite ($HOCl/OCl^-$) and persulfate (PS, $S_2O_8^{2-}$) - have garnered interest. The formation of reactive oxygen species (ROS) involved in the light-driven AOPs is expressed in equations 1-7.

$UVC + TiO_2/rGO \rightarrow e^- + h^+$ (1)

$h^+ + H_2O \rightarrow H^+ + {}^{\cdot}OH$ (2)

$e^- + O_2 \rightarrow O_2^{\cdot-}$ (3)

$UVC + HOCl \rightarrow {}^{\cdot}OH + {}^{\cdot}Cl$ (4)

$UVC + OCl^- \rightarrow {}^{\cdot}O^- + {}^{\cdot}Cl$ (5)

$UVC + H_2O_2 \rightarrow 2\ {}^{\cdot}OH$ (6)

$UVC + S_2O_8^{2-} \rightarrow 2\ SO_4^{\cdot-}$ (7)

Photoreactor engineering is critical to overcome photon and mass transfer limitations that hinder the full implementation of light-driven AOPs. The FluHelik, a tubular photoreactor, facilitates a more homogeneous distribution of radiation and intensifies the dynamics of macromixing [2]. Also, its simple and compact design allows for easy upscaling and industrial application [2]. In this work, a comparative study on the performance of light-driven AOPs over six CECs in secondary-treated urban wastewater was investigated using the FluHelik. CECs included five pharmaceuticals - atenolol (ATNL), venlafaxine (VLX), carbamazepine (CBZ), diclofenac (DCF), sulfamethoxazole (SMX), and the herbicide diuron (DRN). These CECs were subjected to degradation via (i) UVC photolysis, (ii) UVC/TiO_2/rGO photocatalysis, and (iii) photochemical oxidation combining UVC with three different oxidants: H_2O_2, hypochlorite, and PS.

Material and Methods

The FluHelik is an annular channel photoreactor with a concentric quartz tube containing the UVC lamp (Osram Puritec, Hg 6 W). Each phototreatment test was carried out with 1.2 L of secondary-treated urban wastewater, spiked with 200 µg L^{-1} of each compound. Experiments lasted 1 h, with wastewater continuously recirculated from the feed tank to the photoreactor at a flow rate of 70 L h^{-1} using a peristaltic pump. For photocatalysis, 150 mg L^{-1} of TiO_2/rGO, synthesised according to the procedure reported elsewher [3], were added to the system. For photodegradation tests with oxidant addition, an initial dose of 0.6 mM of each

oxidant - H_2O_2, hypochlorite, or PS - was added. CECs were quantified by ultra-high-performance liquid chromatography (UHPLC, Shimadzu Corporation) with tandem mass spectrometry (UHPLC-MS/MS).

Results and Discussion

Figure 1 shows the removal percentage of each CEC after 1 h of phototreatment. The effectiveness of UVC photolysis varied for the CECs tested. DCF, SMX, and DRN were totally removed, as these compounds were not detected in the treated samples. However, UVC photolysis showed limited efficacy in removing the other three compounds (ATNL, VLFX, and CBZ), with degradation levels below 20%. This variation in degradation is consistent with the molar extinction coefficient (ε_λ) and the quantum yield (Φ_λ) associated to each compound, which determine its susceptibility to UVC radiation (λ = 254 nm) [1]. Characterised by $\varepsilon_{254nm} \geq 10^3$ and $\Phi_{254nm} \geq 10^{-2}$, DCF, SMX, and DRN exhibit high susceptibility to UVC photolysis. However, ATNL, CBZ, and VLX demonstrate lower susceptibility, with values of $\varepsilon_{254nm} \leq 10^3$ and $\Phi_{254nm} \leq 10^{-2}$. Hence, other alternatives are needed. Photocatalysis with TiO_2/rGO has been reported to degrade both pharmaceuticals and herbicides in water matrices [3]. Besides the effective removal of DCF, SMX, and DRN, there was no improvement in the degradation of the remaining CECs compared to the process based only on UVC photolysis. Further optimisation may be required to improve the photocatalytic performance. In photodegradation tests with oxidant addition, beyond the removal of the CECs susceptible to UVC photolysis, considerable levels of degradation were also achieved for the others CECs.

In the UVC/chlorine process, removal ≥ 60% was obtained for ATNL, CBZ, and VLX, while in the UVC/H_2O_2 and UVC/PS processes, all target CECs were removed by at least 80%. As described in equations 4-7, different ROS are generated depending on the oxidant applied, each presenting different reactivity towards CECs and also towards other compounds present in wastewater matrices.

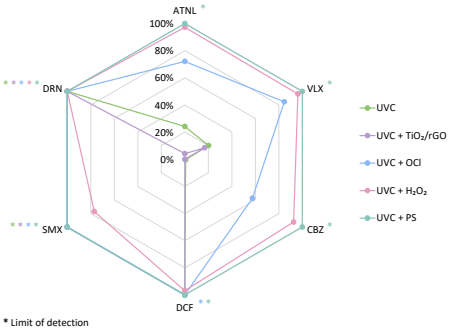

Figure 1. CECs percentage removal after 1 h of treatment for the different photochemical processes.

These results suggest that UVC/H_2O_2 and UVC/PS are the most suitable processes for removing the target CECs in urban wastewater after secondary treatment. A preliminary comparison of the operating costs associated with UVC/H_2O_2 and UVC/PS highlights that, at equimolar doses, the cost of PS is about 10 times higher than that of H_2O_2 [1]. However, from an operational point of view, PS offers advantages in terms of safety during transport, handling and storage, with associated cost savings [1].

Conclusions

This study demonstrates the effectiveness of light-driven AOPs, particularly the combination of UVC radiation with oxidants, in mitigating the presence of CECs in secondary-treated urban wastewater. Employing the FluHelik photoreactor, the phototreatment processes ranked as follows for the removal of the six target CECs: UVC photolysis ≈ TiO_2/rGO photocatalysis < UVC/chlorine < UVC/H_2O_2 ≈ UVC/PS. Combining UVC with H_2O_2 or PS removes at least 80% of all the target CECs in 1 h of treatment.

Acknowledgments

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