Solar photodegradation of pharmaceutical compounds in surface water from an urbanized reservoir using a FluHelik reactor

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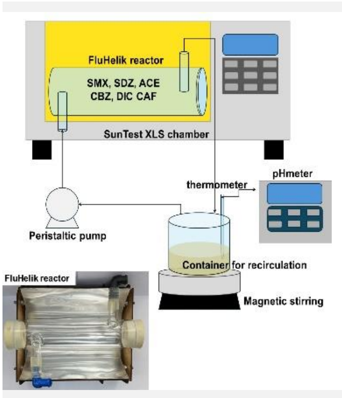

Surface water is a potential receptor of contaminants of emerging concern (CECs), including pharmaceutical drugs. Furthermore, wastewater treatment plant (WWTP) systems are not designed to remove emerging contaminants. Thus, it is essential to develop alternatives technologies for the degradation of CECs. The main objective of this study is to assess the feasibility of a FluHelik reactor for this purpose using a solar simulator chamber set at radiation conditions similar to those observed in Minas Gerais, Brazil. In this context, FluHelik photoreactor was used to evaluate the removal of six pharmaceutical compounds (sulfamethoxazole, sulfadiazine, acetaminophen, carbamazepine, diclofenac and caffeine) in surface water from an urbanized reservoir located between three municipalities (Ibirité, Sarzedo and Betim). After 4 hours of photodegradation, removal of diclofenac and sulfadiazine were >90% and 22%, respectively, and negligible for all other CECs in the conditions evaluated in this study.

Introduction

Pharmaceutical compounds are an important class of contaminants of emerging concern (CECs). They are commonly found in aqueous environmental matrices (surface, underground, drinking and commercial waters, wastewater effluents) at low concentrations (µg and ng L^{-1}) [1]. Several studies worldwide have reported occurrences, fate, and hazards associated with these CECs for aquatic ecosystems and human health [2]. In this context, marked by potential environmental risks due to the deterioration of water bodies caused by poor sanitation, mainly in low-income countries, different studies have devoted their efforts to the identification and removal of CECs. Many studies based on advanced oxidative processes (AOPs) for the removal of pharmaceutical compounds have been carried out in the past years [3].
In this context, technologies based on light irradiation, such as photodegradation, have gained attention for the degradation of recalcitrant contaminants in different water matrices [4]. The removal can occur by direct and indirect photolysis. In direct photolysis, contaminants absorb radiation directly and go through various photodegradation pathways, depending on their chemical structure. Direct absorption of solar radiation can be enhanced by the presence of functional groups that absorb light, known as photosensitizers, resulting in indirect photolysis [5]. Photodegradation is essential for natural removal of CECs, where solar irradiation (i.e. UV and visible light) is abundant during daylight hours. However, this process can be optimized to increase the use of solar radiation, resulting in higher removal efficiencies. One path to promote photodegradation is the application of innovative reactors, such as the FluHelik, which enables intense agitation dynamics and homogeneous radiation distribution [6]. Thus, the aim of this study was to assess the removal of selected pharmaceutical compounds in surface water from an urbanized reservoir by photodegradation using a FluHelik reactor under solar irradiation. Six multiple-class drugs (sulfamethoxazole - SMX, sulfadiazine - SDZ, acetaminophen - ACE, carbamazepine - CBZ, diclofenac - DIC and caffeine CAF) were selected due to their high human and veterinary usage worldwide.

Material and Methods

The photodegradation process was with surface water sampled (1L) at an urban lake located between three municipalities (Ibirité, Sarzedo and Betim) in Minas Gerais State, Brazil. The surface water showed the following characteristics: nitrate = 3.4 mg L^{-1}, nitrite = 0.12 mg L^{-1}, phosphate = 3.2 mg L^{-1}, chemical oxygen demand (COD) = 62 mg L^{-1}, hardness (74.58 mg $CaCO_3$ L^{-1}).
All CECs (high purity grade, >95%) were acquired from Sigma- Aldrich and were used to prepare the stock solution in HPLC methanol grade (500 mg L^{-1}). Working standard solutions were prepared to spike surface water samples with 100 µg L^{-1} of each compound. Analytical curves were built based on nine concentrations (5, 10, 25, 50, 75, 100, 125 and 150 µg L^{-1}) injected in duplicates in High-Performance Liquid Chromatography with Diode Array Detection (HPLC-DAD LC2040C Nexera-Shimadzu). Then, target CECs were quantified using this same analytical method.
Reactions were performed in a FluHelik reactor (430 mL of volume and 75 L h^{-1} of recirculation flow rate) produced in borosilicate coupled to a parabolical concentrator placed inside a solar simulator chamber (SUNTEST CPS+, ATLAS) set at 268 W m^{-2} (330–800 nm) which is equivalent to

30 W m^{-2} (300–400 nm; similar average radiation to those observed in Minas Gerais, Brazil, Latitude: 19° 48' 57" South, Longitude: 43° 57' 15" West). Photodegradation was carried out for 4 hours. The solution pH was monitored, and aliquots were retained to check degradation over time.

Results and Discussion

Analytical methods applied in this study were satisfactory as the coefficient of determination (R^2) was higher than 0.99 for all CECs (Table 1). After the applied photodegradation process, removal of DIC and SDZ were >90% and 22%, respectively, as shown in Figure 1a. However, the main process for removal of DIC was direct photolysis (Figure 1b). The removal of the other CECs were insignificant under conditions evaluated in the present study. Espíndola et al. (2024) assessed the removal of eight CECs using FluHelik photoreactor (UVC/H_2O_2 process) and the system was able to removal all CECs at concentrations below the limit of detection [6] probably due to the formation of oxidative radicals via photolysis of H_2O_2. Despite our results, technologies based on FluHelik photoreactors might be a promising alternative for the removal of CECs.

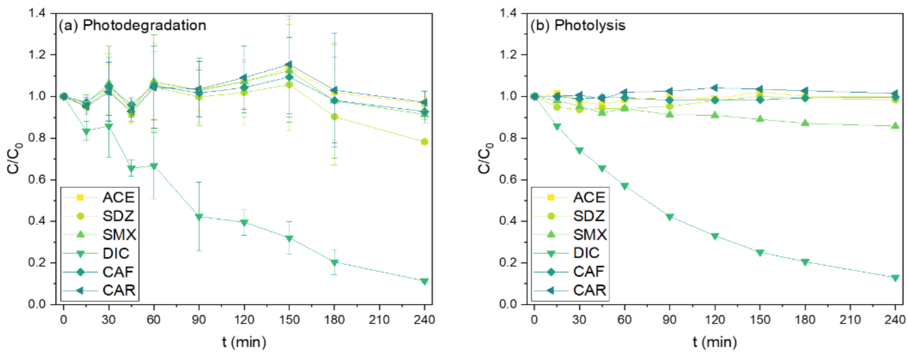

Figure 1. Removal of selected pharmaceutical compounds. Error bars represent standard deviation (n= 2).

Table 1. HPLC-DAD parameters and selectivity and linearity.

CECs	RT[a] (min)	Chanel (nm)	Regression Equation	R^2
ACE	6.62	243	y = 995.3x + 234.46	0.9992
CAF	7.56	272	y = 678.05x - 69.204	0.9990
SDZ	7.72	269	y = 847.66x + 876.38	0.9988
SMX	9.82	269	y = 819.71x + 1837.2	0.9980
CAR	11.19	285	y = 995.3x + 234.46	0.9995
DIC	14.61	269	y = 364.46x + 339.28	0.9985

[a] RT = retention time.

Conclusions

The FluHelik reactor provided a slight increase on SDZ photodegradation from complex matrix compared to photolysis. Further studies are essential to better understand the removal mechanisms of SDZ and other CEC's by FluHelik reactor.

Acknowledgments

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