Low-cost photoreactor used in the degradation of Diuron and 2,4-D herbicides by photolysis, ozonation and ozonation with UVC light

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In this study, a low-cost photoreactor was created and, combined with an ozone generator, was used to degrade the herbicides Diuron (DRN) and 2,4-D. The processes of direct photolysis, alkaline ozonation and alkaline ozonation with UVC light were evaluated. Treatment efficiencies followed the sequence: DRN/O_3/UVC/pH9 > DRN/-/UVC/pH9 > DRN/O_3/-/pH9 and 2,4-D/O_3/-/pH9 > 2,4-D/ O_3/UVC/pH9. Direct photolysis of 2,4-D did not occur. A first-order kinetic model was adjusted, with a kinetic constant of 0.044 min^{-1} for the DRN/O_3/UVC/pH9 process and 0.098 min^{-1} in the 2,4-D/O_3/-/pH9 process. The final scans, in the UV light range, obtained after the best treatments for each case, did not show the characteristic peaks of the two herbicides. The photoreactor had a total cost of R$ 312.00 and the treatment cost, calculated as Electrical Energy per Order (EEO) was 46.12 kWh/m^3/order, for Diuron and 12.98 kWh/m^3/order, for 2,4-D.

Introduction

Diuron (DRN) and 2,4-D are herbicides used on a large scale in agriculture, have toxic behavior and have been frequently detected in various aquatic matrices [1]. Therefore, developing efficient and technically and economically viable treatment methods for the degradation of these contaminants is essential. This work aimed to manufacture a low-cost photoreactor that, combined with an ozone generator, was applied to the degradation of the herbicides Diuron and 2,4-D. The direct photolysis processes with UVC light, ozone and UVC irradiation (O_3/UVC) and O_3 in an alkaline medium were evaluated.

Material and Methods

The photoreactor consisted of an external polyvinyl chloride - PVC tube (40 mm), an internal 304 stainless steel tube (33.40 mm) and PVC connections that join the external tube to two hoses for the inlet and outlet of the solution. A UVC lamp was installed in the center of the inner tube (HNS 30 W G13 from Osram, λ_{max}=254 nm). The reaction system is composed of the photoreactor, the ozone generator (Ozonio Line) and a closed glass container (3.2 L), with 4 inlets; two for the gas and two for the aqueous solution. The mixture, oxygen and ozone, with a flow of 150 mL.min^{-1} and O_3 concentration of 70 µg.mL^{-1} was introduced into the closed container throughout the experiment. At the exit, a catalyst was installed to destroy residual ozone. A submersible pump with a flow rate of 150 L.h^{-1} (BOYU - Model: SP-500) recirculates the solution through the photoreactor.

Procedimento experimental

The analysis of herbicides in the aqueous solution was carried out using a UV-Vis spectrophotometer (UV-1280, Shi-madzu), at wavelengths of 248 nm for Diuron and 284 nm for 2,4-D. In experiments with irradiation, the UVC lamp was previously heated for 30 minutes. 2 L of solution with an initial herbicide concentration of 5 mg.L^{-1} was continuously recirculated through the photoreactor. In all experiments, the initial pH of the aqueous solution was adjusted to 9.0 with a 1 mol.L^{-1} NaOH solution. The beginning of the reaction corresponded to the moment the ozonizer was turned on. Samples were collected at 0, 2, 4, 6, 10, 15, 20, 30, 60 and 90 minutes of reaction. After each collection, the samples were filtered through 12.5 cm filter paper (Unifil) and subjected to vacuum for 20 minutes to eliminate residual dissolved O_3. The effectiveness of the degradation process was accompanied by a reduction in the concentration of herbicides in solution. In the most efficient method for each herbicide, the samples were analyzed by the High Performance Liquid Chromatograph with UV detector (HPLC/UV, High Performance Liquid Chromato-graphy), from Thermo Scientific.

Electrical Energy Per Order (EEO) was used to calculate the electrical energy consumption for the degradation of herbicides [2].

Results and Discussion

Figure 1 (a) and (b) shows the degradation kinetics of the herbicides DRN and 2,4-D, by the evaluated processes. The values of the first-order apparent kinetic constants of the reaction and the percentages of degradation in 90 minutes are shown in Table 1. Figure 2 (a) and (b) shows the UV-Vis Spectra of the samples, obtained before and after the degradation of the herbicides DRN and 2,4-D.

Figure 1. $C_{(t)}/C_{(0)}$ of DRN end 2,4-D.

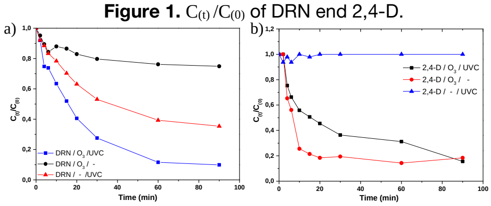


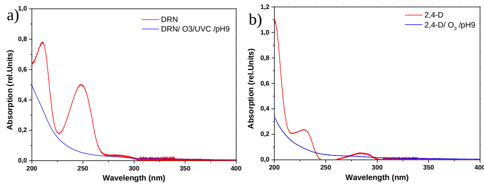
Table 1. Kinetic constant and percentage of herbicide degradation.

Process	Diuron		2,4-D	
	***k*, min.$^{-1}$**	**Degrad, %**	***k*, min.$^{-1}$**	**Degrad, %**
O_3/UVC/pH 9	0.0441	90%	0.0456	84%
O_3/ - /pH 9	0.0088	25%	0.0976	82%
- /UVC/pH 9	0.0224	65%	-	0%

The results reveal that the most efficient process in the degradation of Diuron was alkaline oxidation with UVC light (O_3/UVC/pH9). Photolysis made a significant contribution to the degradation of Diuron, with a rate of 65% and a kinetic constant of 0.0224 min^{-1}. This occurs because the absorption spectrum of Diuron's electromagnetic radiation coincides with the emission spectrum of the lamp used. This result is in agreement with the work of [3], who evaluated the photolysis of Diuron by solar irradiation. In that work, direct photolysis was favored with low pH values (<2) and low concentrations of Diuron (4.9 mg.L^{-1}), however, the degradation of Diuron by photolysis led to the formation of byproducts, such as 1-(3,4-dichlorophenyl)-3-methylurea.

Regarding the degradation of the 2,4-D herbicide, alkaline ozonation (with the lamp turned off) proved to be the fastest and most favorable process for eliminating this contaminant. The obtained value of the first-order apparent kinetic constant was 0.0976 l.min^{-1}. This result is in agreement with the work of [4], who observed a high reactivity of 2,4-D with ozone in the ozonization process at alkaline pH. It is important to highlight that there was no degradation of 2,4-D by UVC photolysis, this is explained by the non-absorption of the electromagnetic energy of 2,4-D at 254nm.

Figure 2. the UV-Vis Spectra of DRN and 2,4-D before and after treatments.



A change in the profile of the absorption curves of the two herbicides was observed after the applied treatments. The characteristic peaks of Diuron (at 211 and 248 nm) and 2,4-D (at 284 and 228 nm) practically disappeared after the treatments.

HPLC/UV analysis was carried out on the aqueous solutions obtained after treatment; Diuron presented a peak retention time of 8.50 minutes and 2,4-D, at 4.75 minutes, both achieved an area reduction of approximately 99% after treatment.

The total cost of the photoreactor built was R$ 312.00 and the treatment cost, calculated as Electrical Energy per Order (EEO) was 46.12 kWh/m^3/order, for Diuron and 12.98 kWh/m^3/order, for 2,4-D.

Conclusions

Alkaline oxidation with UVC light and alkaline ozonization were the most efficient processes in the degradation of the herbicides Diuron and 2,4-D, respectively. The photoreactor developed together with the ozonizer proved to be an effective and economical alternative for the degradation of these herbicides.

References

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