

Hydrochlorothiazide Degradation by UV-based Advanced Oxidation Processes



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Introduction

Most of pharmaceutical products are considered as emergent pollutants. This represents a growing concern, especially in developed countries, where they are frequently used. Water waste treatment plants degrade partially these pollutants while others remain unaltered and are detected in the plant effluents, as it was reported in numerous studies [1,2]. Hydrochlorothiazide (HCTZ), a thiazide diuretic frequently used in the treatment of hypertension, appears as one of the twenty most detected and persistent compound in wastewater tributaries in Spain, Canada and Netherlands [3].

Conventional biological treatments have not demonstrated to be effective to remove this pollutant in wastewaters. The AOPS (Advanced Oxidation Processes) represent an innovative alternative technology to eliminate these resistant compounds. Moreover, the combination of direct photolysis (UV radiation) with oxidant species such as HO• or SO₄⁻ radicals has been successfully applied to destruct organic micropollutants in different water matrices [4].

The main objective of this study was to analyse the efficiency of ultraviolet (UV) and solar radiation in the photodegradation of hydrochlorothiazide. For this reason, it is determined:

- Quantum yield and photochemical kinetic parameters of the process were determined by UV photolysis of HCTZ with the influence of the different operational variables (initial concentration and pH),
- Indirect photodegradation in presence of HO• radical promoter and
- by-products toxicity.

Materials and Methods

UV photolysis experiments were conducted using a photochemical reactor equipped with a low-pressure mercury lamp which emitted monochromatic radiation at 254nm was used.

The influence of operational variables was investigating evaluating the effect of different initial pH (3,8.5 and 10) and the influence of concentration (25, 15 and 10ppm HCTZ). Additionally, in order to evaluate the effect of HO• radical, hydrogen peroxide was added at initial concentrations of 3, 5, 7 and 10 ppm. HCTZ concentrations were measured by HPLC (Novapak C18 column). The detection was performed at 310nm using a mobile phase of acetonitrile and formic acid (70:30 in volume), the elution flow rate was 0.35mL min⁻¹ and the injection volume was 100uL in all samples.

By-products cytotoxicity were evaluated by using an MTS assay to determine the % viability of human embryo kidney cells (HEK-293) from the CIC cell bank of the University of Granada. Degradation kinetics were first studied in the presence of phosphate buffered saline (PBS), and 10,000 HEK-293 cells were then incubated for 24h, subsequently changing the medium and adding HCTZ by-products (10:100µL dilution); after incubation for a further 24h, 20µL MTS was added and its absorbance was measured at 2h using INFINITENANOQUA equipment, with a sample reading of 9 times at 490nm absorbance.

Results and Discussion

UV direct photolysis results showed a 90% reduction of the initial concentration of HCTZ after 30min, as it is observed in Figure 1. The values obtained are like those reported by other authors for other pharmaceutical compounds [5,6]. As it was expected, the obtained results in presence of HO• radical improved the treatment reaching a complete degradation after only 20min (Figure 1). However, the unique presence of radical promoters does not show any effect. The apparent reaction rate constant also increases with the addition of H₂O₂ (Table 1) due to the generation of HO• which attack HCTZ by degrading it into by-products of smaller molecular weight. The low molar absorption coefficient of H₂O₂ could be compensated by increasing the amount of reagent, however, HO• radicals generated can also react with

H₂O₂, especially if it is in high concentrations. The reaction rate constant of HO• with HCTZ was determined to identify the influence of these recombination reactions, obtaining a value of

kHCTZ/HO•=6.43x10⁹ M⁻¹s⁻¹, higher than the reaction rate constant of HO• (3.3x10⁷ M⁻¹s⁻¹). Therefore, degradation of HCTZ by HO• may be favoured until a given initial concentration of H₂O₂.

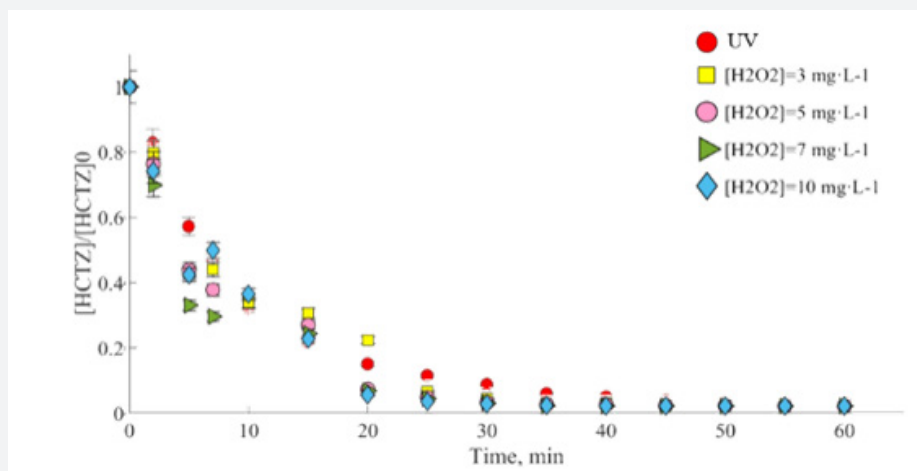


Figure 1: Variation in the relative concentration of HCTZ as a function of the irradiation time at different initial concentrations of H₂O₂.

Operational variables studied showed the following results: Photodegradation rate decreases as HCTZ initial concentration increases due to the energy absorbed by each molecule. The ef-

fect of the initial pH pointed out an increase of degradation rate at acidic pHs, which is in accordance with the speciation of HCTZ.

Table 1: Parameters obtained from the different experiments.

	Direct Photolysis		K (S ⁻¹)	K' _E (m ² . Eins ⁻¹)	R ₂₅₄ (%)	T1/2 (s)
				0.0019	0.0132	18.5
Variables	pH	3	0.003	29.21	0.02	231.05
		8.5	0.0022	21.42	0.02	315.07
		10	0.0018	17.53	0.01	385.08
	Concentration	25ppm	0.0014	16.55	0.01	495.11
		15ppm	0.0017	13.63	0.01	407.73
		10ppm	0.002	17.53	0.01	385.08
	HO• Radical	8.8.10 ⁻³ mol. L ⁻¹	0.0013	12.66	0.01	533.19
		1.5.10 ⁻⁴ mol. L ⁻¹	0.0019	18.5	0.02	364.81
		2.1.10 ⁻⁴ mol. L ⁻¹	0.0021	20.45	0.02	330.07
2.1.10 ⁻⁴ mol. L ⁻¹		0.0029	28.24	0.02	239.02	

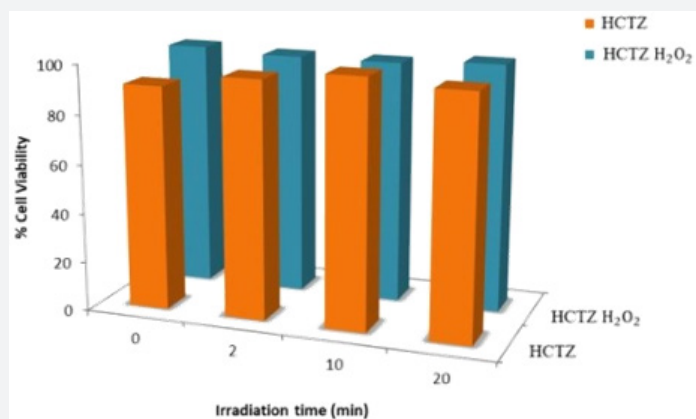


Figure 2: HEK-293 % Cell viability in the different HCTZ experiments after different periods of UVC radiation. [HCTZ]₀= 15mg L⁻¹, [H₂O₂]=2.9·10⁻⁴ M.

Table 1 depicts the obtained HCTZ quantum yield as a function of their concentration (25, 15, and 10mg·L⁻¹ respectively), pointing out that HCTZ photodegradation rate decrease as concentration increases, due to the energy absorbed by each molecule. Hence, given that the radiation energy irradiated in the medium per unit of volume is constant, HCTZ molecules can accept more radiant energy at lower concentrations, explaining the behavior observed.

The comparison of the viability of by-product treated cell cultures with the viability of original product treated cell cultures (time 0) (Figure 2) showed a greater viability of the by-product treated cells, reason why these products are considered less toxic than the original product.

Conclusion

The results obtained in this study suggested that direct photolysis by UV photolysis is not sufficiently effective to reach the complete degradation of this drug. The operational variables play an important role in the design of the process, as well as, the addition of HO radical promoter, which in presence of UV radiation enhancing the degradation process. Moreover, the degradation by-products obtained are not toxic. Consequently, this

procedure could be a promising technology for HCTZ degradation in waste waters.

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