

## Research Article

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# Solar photodegradation of carbamazepine from aqueous solutions using a compound parabolic concentrator equipped with a sun tracking system

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**Abstract:** The primary purpose of this study was to investigate the efficiency of a Compound Parabolic Concentrator (CPC) equipped with a sun tracking system in the photolysis of carbamazepine as a refractory organic compound. The natural sunlight experiments were accomplished during the period May–July 2017 in Tehran, Iran. The intermediate by-products of the process of solar photodegradation of carbamazepine (CBZ) were characterized using LC–MS. The results showed that increasing the reactor temperature did not significantly change CBZ degradation efficiency. However, the solution pH played a comparatively important role in CBZ solar photo degradation: removal efficiency increased considerably with pH from about 49% at pH 7 to almost 61% at pH 9. According to our findings, using a CPC reactor equipped with a sun tracker system promotes the solar photo-transformation rate of CBZ by 2–3 fold. In addition, LC/MS analysis showed that eight main intermediates were formed in the treated solution after solar photodegradation of CBZ. Therefore, complete mineralization of CBZ was not accomplished.

**Keywords:** CPCs; Pharmaceutical residues; Phototransformation pathways; Sun tracker.

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## 1 Introduction

Pharmaceutical residues in bodies of water are a serious concern due to their abundance, recalcitrance, and chronic effects [1]. Treated wastewater effluents are significant sources of pharmaceuticals residues in bodies of water, because most of these compounds are refractory to conventional wastewater treatment [2–5]. Due to the generally lower concentrations and cost, it is technically impossible to monitor all of these compounds in water and wastewater. Thus, the use of some pharmaceuticals as indicators has become popular [6]. Carbamazepine (CBZ), an antiepileptic pharmaceutical compound, is usually used as an indicator to confirm the presence of drugs in aqueous environments [7]. It is commonly detected in receiving waters and bodies of water and is one of the most recalcitrant pharmaceutical compounds to biodegradation (less than 10% is typically removed during wastewater treatment) [5]. This compound also is exceptionally resistant to photodegradation (with a half-life of more than 100 days) [8, 9].

Recent studies have attempted to develop simple, reliable, high-throughput and inexpensive treatment methods for the removal of pharmaceutical residues from aqueous environments. In many new advanced wastewater treatment processes, artificial UV radiation plays a key role in the removal of micropollutants, especially in combination with other chemical agents. It was largely used because of its great oxidation potential which could degrade refractory organic pollutants to biodegradable products or carbon dioxide directly or indirectly [10–13]. However, the energy and safety requirements severely limit the use of artificial UV irradiation. These restrictions could be partially overcome by using solar radiation instead of artificial UV.

Solar photodegradation has been known as one of the most effectual treatment methods for emerging pollutants [14]. Solar irradiation is a broadly available renewable energy source [15]. At the

current energy consumption rate, the solar energy received by Earth in one hour can supply the world's energy requirements for more than a year [16]. The situation is even better in sunny countries like Iran, which experiences approximately 300 cloudless days in a year and an average 2200 kWh/m<sup>2</sup> solar radiation per year [17]. Using the sun as an energy source is a good option for the reduction of conventional energy consumption costs of wastewater treatment and is environmentally attractive [18, 19]. But solar radiation bands contains low UV light and are not constant in the natural environment due to fluctuations of diurnal and seasonal cycles; therefore, direct and uncorrected use of solar irradiation would not be successful in water and wastewater treatments processes [20].

Although some studies have been done to reduce these limitations, few studies have focused on the use of Compound Parabolic Concentrator reactors (CPCs) with or without equipped solar tracking systems in water and wastewater treatment [21, 22]. Some of these reactors can concentrate sunlight between 5 and 50 times [23]. CPC reactors equipped with solar tracking systems can continuously concentrate sunlight into the focal line. Collecting solar radiation from all directions in the atmosphere with high efficiency and simple construction and operation are important advantages of these reactors [18]. It is reported that this method can be very effective for the treatment of emerging pollutants as well as for disinfection [24]. Lam and Mabury [25] report that CBZ photodegradation is an important removal process in surface waters and photolysis products were less recalcitrant than mother compound.

With this background, the main purpose of this work was to study the efficiency of a Compound Parabolic Concentrator (CPC) equipped with a two-axis (horizontal and vertical) tracking system in the photolysis of carbamazepine (CBZ) as a pharmaceutical residues indicator.

## 2 Materials and Methods

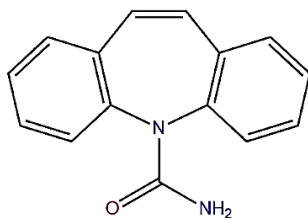
### 2.1 Materials

Carbamazepine (CBZ  $\geq 99\%$ ) was acquired from Arasto Pharmaceutical Chemicals Inc. (Tehran, Iran). The chemical structure and specification of CBZ are shown in Figure 1. All other used chemicals in this study, such as hydrochloric acid and sodium hydroxide, was purchased from Merck, Darmstadt, Germany.

### 2.2 Installation and Experimental procedure

A schematic diagram of the experimental pilot CPC reactor equipped with sun tracker system is shown in Figure 2. The pilot consisted of a quartz tube (number 1 in Figure 2) with a length of 80 cm, an outside diameter of 3.2 cm and inside diameter of 2.8 cm; a compound parabolic collector (CPC) (number 2 in Figure 2); and a dual axis solar tracker system. The CPC aperture area was 0.38 m<sup>2</sup>. The tracking system pursues the angular height position of the sun in the sky in addition to pursuing the sun's east-west motion by rotating the CPC reactor. As shown in Figure 2, the solar tracker system has a photo sensor (number 3 in Figure 2), a vertical rotator (number 4 in Figure 2), a horizontal rotator (number 5 in Figure 2), and a controller (number 6 in Figure 2). The rotators are principally conducting the action of sun tracking. The horizontal rotator tracks the east-west movement of the sun, and the vertical rotator tracks the sun's up-down motion. These rotators and the photo sensor are interfaced with a controller, which is controlling the rotators according to the sensor's input. The photo sensor uses a light-dependent resistor (LDR) to acquire the sun's position. The LDR sensor senses the light intensity and sends a signal to the controller. The controller compares the signals received from the photo sensor and decides the rotation direction of the rotators according to the stored program.

The reactor temperature was recorded at the beginning and end of the reaction using a mercury thermometer (number 7 in Figure 2) placed inside the quartz tube. To determine the role of temperature in the removal of carbamazepine, a black copper rod (number 8 in Figure 2) was placed inside the quartz tube. The reactor without the black copper tube was called CPC<sub>1</sub>, while the reactor with the tube was called CPC<sub>2</sub>. The CPC (1 and 2) experiments were replicated with the same CPC and tracking system but one different days and with different quartz tubes (with or without the copper rod). The conditions on the different days were similar (sunny and calm). As a negative control for the effect of CPC on CBZ removal, a simple quartz tube without CPC or copper rod was used (this situation is termed the "blank"). Natural sunlight experiments were carried out during three consecutive weeks during the period of May–July 2017 at the University of Shahid Beheshti University of Medical Sciences in Iran, local latitude 35° 47' 50" N, longitude 51° 23' 50" E.



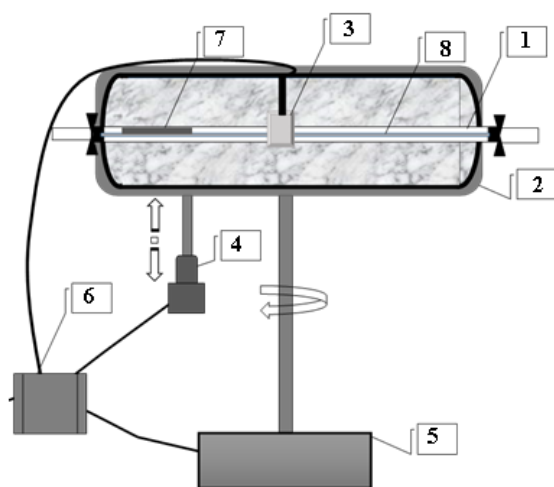
Carbamazepine

Chemical Formula:  $C_{15}H_{12}N_2O$ 

Molecular Weight: 236/27

m/z: 236.09 (100.0%), 237.10 (16.2%), 238.10 (1.2%)

Elemental Analysis: C, 76.25; H, 5.12; N, 11.86; O, 6.77

**Figure 1:** Chemical structure and specifications of Carbamazepine.**Figure 2:** Schematic diagram of pilot scale CPC with tracking system reactor; 1- quartz tube (with inlet and outlet valves), 2 - CPC, 3 - photo sensor, 4 - Vertical rotator, 5 - Horizontal rotator, 6 - Controller, 7 - Thermometer, 8 - Copper rod

## 2.3 Solar radiation dose

In this study, the solar light intensity and the reactor's temperature changes were measured and recorded. Solar irradiance was measured with a global radiometer (Model HAGNER, Sweden). To estimate the solar radiation dose, the cumulative solar radiation dose (CSRD) into the reactor over the period of experiment per unit time and volume was calculated. The CSRD was calculated by integrating the average of measured solar irradiance ( $Q$ ) during the different exposure times using following equation:

$$CSRD = \frac{C}{1000} \frac{A}{V} \int_{t_{start}}^{t_{end}} Q dt \quad (1)$$

where CSRD is cumulative solar radiation dose (kWh/L),  $C$  is reflection coefficient (typically 0.8),  $A$  is the CPC aperture area ( $m^2$ ),  $V$  is the volume of treated wastewater (L) and  $Q$  is the measured solar irradiance ( $W/m^2$ ).

## 2.4 CBZ-contaminated water preparation

A standard stock solution of CBZ (150mg/L) was prepared from analytical grade CBZ powder and methanol/deionized water (20% volume/volume). This solution was stored in the refrigerator at 7°C for further use and refreshed at 5-day intervals. The stock solution of CBZ was spiked into the reaction solution in a 500 mL volumetric flask to yield a selected concentration from 0 (control) to 5 mg/L with intervals of 0.5 mg/L. Generally, the volumetric percentage of methanol present in reaction solutions was less than 0.1% (v/v). The solution pH was adjusted with 0.01N  $H_2SO_4$  and 0.01N NaOH. CBZ removal experiments were carried out according to the following approaches: (1) Blank reactor (quartz tube without CPC, tracking system and copper rod), (2)  $CPC_1$  reactor (quartz tube in the focal axis of CPC) and (3)  $CPC_2$  reactor ( $CPC_1$  plus copper rod to quartz tube). All experiments were performed in duplicate.

## 2.5 Analytical methods

CBZ concentration measurements were carried out by HPLC (Knauer) equipped with an Eclipse plus C18 column ( $3.5 \times 4.6 \times 100$  mm) and a UV detector at  $\lambda = 280$  nm. Its retention time (RT) was  $7.2 \pm 0.1$  min. A mixture of methanol/water solution (60/40 %v/v) was used as the mobile phase at a flow rate of 0.8 mL/min, and the injection volume was 20  $\mu$ L. The lowest detection and quantification limits were estimated to be approximately 50  $\mu$ g/L and 100  $\mu$ g/L respectively. CBZ products in photochemical reactions were also monitored by liquid chromatography mass spectrometry (LC-MS, Quattro Micro API micro-mass Waters 2695) with a Thermo Quest Finnigan LCQ Duo mass spectrometer system.

Ethical approval: The conducted research is not related to either human or animal use.

## 3 Results and Discussion

Results were classified into four main sections: (1) Solar radiation, (2) Effect of initial CBZ concentrations, (3)

Effect of pH and Temperature, and (4) CBZ transformation products and pathway.

### 3.1 Solar radiation

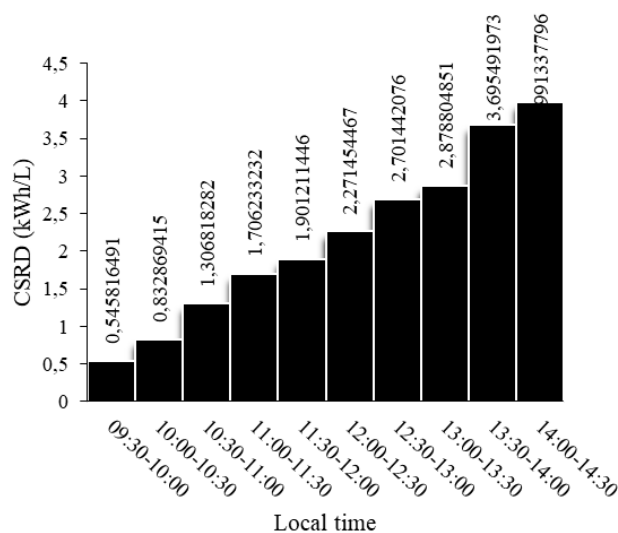
The cumulative solar radiation doses (CSRD) over the period of experiments are shown in Figure 3. The CSRD values were calculated using equation (1). As shown in this Figure, the solar radiation doses fell within the range of 0.5 to 4 kWh/L.

### 3.2 Effect of initial CBZ concentrations

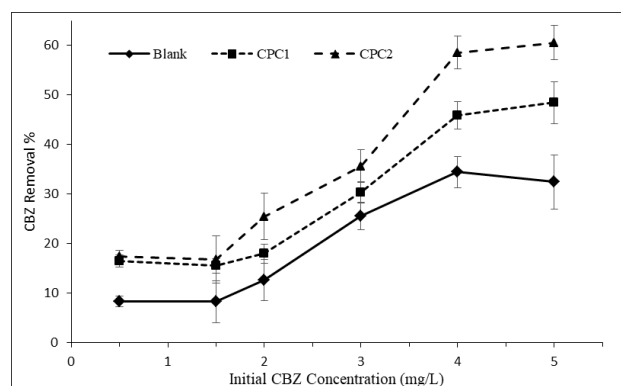
The efficiency of removal of CBZ during exposure to three hours of sunlight (10:30-13:30) at pH  $7 \pm 0.01$  is shown in Figure 4. As can be seen in this Figure, there was no significant change in the phototransformation rate of CBZ with the initial concentrations of 0.5 mg/L to 2 mg/L. When the initial concentration was increased from 2 to 4 mg/L, the phototransformation rate of CBZ has increased remarkably in all three reactors (blank, CPC1, and CPC2), after which the trend was invariant. These results suggest that the CBZ phototransformation reactions follow pseudo-first-order kinetics. Also, these observations may be explained by the exposure of specific binding sites of CBZ at higher concentrations, assuming that binding sites were limiting. It is also seen in Figure 4 that conversion rates in CPC1 and CPC2 reactors are about twice as high as that for the blank reactor. Therefore, it can be concluded that concentrating solar radiation and use of the sun tracking system could dramatically increase CBZ removal efficiency. However, there is no significant difference in CBZ removal between CPC1 and CPC2, despite the higher temperature induced by the presence of the copper rod in CPC2. It thus seems that temperature has little effect on CBZ removal.

### 3.3 Effect of pH and Temperature

Solution pH significantly affects the photolysis of organic contaminants, including the nature of photoproducts as well as reaction kinetics [26, 27]. The effects of pH and temperature variation during CBZ solar photolysis by CPC1, CPC2, and blank reactors are shown in Figure 5. As shown in Figure 5a, in all three reactors, the CBZ removal rate is low at low pH. However, there is a significant difference in the removal efficiency of CPC1 and CPC2 reactors relative to the blank reactor under all three pH conditions. This



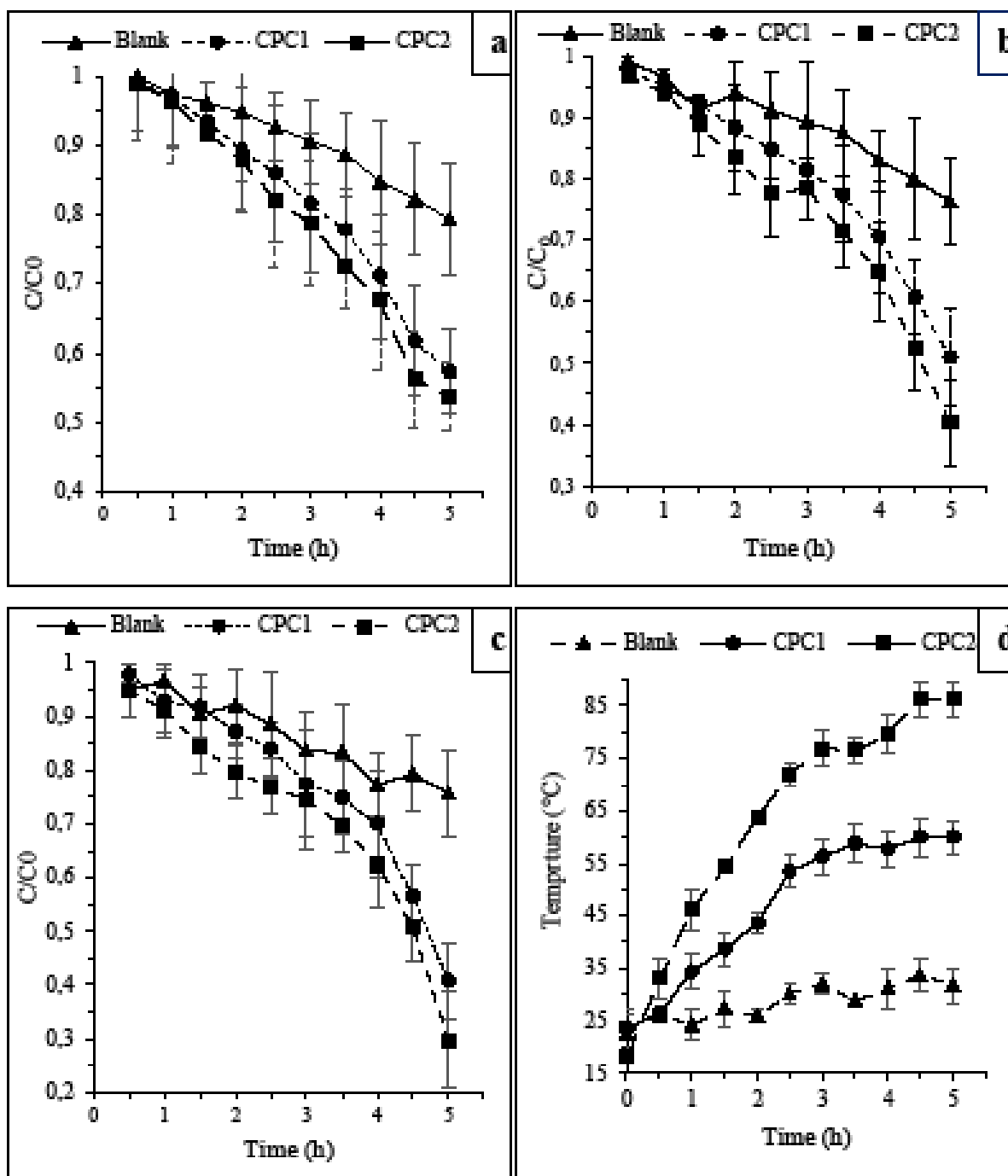
**Figure 3:** Estimated cumulative solar radiation dose (CSRD) in the period of experiments into the reactor per unit of time and volume.



**Figure 4:** Effect of initial CBZ concentrations on removal efficiency in three reactors (solar irradiation time 3 hours (10:30-13:30) pH =  $7 \pm 0.01$ ).

further shows that the concentration of solar radiation by CPC reflectors dramatically increases the effectiveness of CBZ removal. However, the efficiency of the blank reactor in CBZ removal is higher than that previously reported for similar conditions (see refs. [28] and [29]). This difference is likely due to the different initial CBZ concentrations and differences in solar radiation angles. Upon increasing the pH to neutral and basic, the efficiency of CBZ removal was enhanced in all three reactors (see Figure 5b and c). Thus, solution pH played an important role in CBZ photodegradation, as removal efficiency increased slightly with pH from about 49% at pH 7 to almost 61% at pH 9.

Although temperature differences between CPC1 and CPC2 reactors were significant (Figure 4 d), there is no



**Figure 5:** Comparison of the Efficiency of Blank, CPC1 and CPC<sub>2</sub> reactors in removal of Carbamazepine (Mean ± SD) at contact Time of 0.5 to 5 hours - start time: 9:30 a.m., end time 2:30 p.m. Initial CBZ concentration = 3 mg/L (a) pH= 4± 0.1; (b) pH=7± 0.1; (c) pH= 9± 0.1 and (d) Temperature variations in these reactors.

meaningful difference in removal efficiency between the two reactors. From the results above, it seems that the temperature has a minor effect on CBZ removal efficiency. This is consistent with other published findings [30, 31].

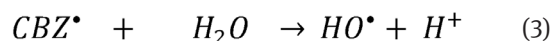
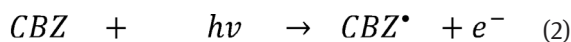
As can be seen in Figure 5, using a CPC reactor equipped with sun tracking system promote CBZ transformation by 2-3 folds higher than without CPC and sun tracking system.



### 3.4 CBZ transformation products and pathway

Solar photodegradation reactions can occur directly or indirectly. In direct photodegradation, solar radiation received by the compound itself leads to phototransformations; in indirect photodegradation, highly reactive radicals, such as atomic oxygen and hydroxyl radicals ( $\text{HO}^\bullet$ ), are generated using catalysts [32, 4].

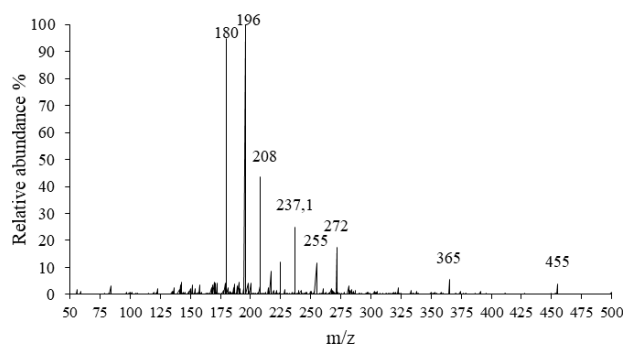
The direct solar photodegradation of CBZ starts after absorption of photons from solar radiation by the compound. The interaction between sunlight and CBZ leads to the generation of hydroxyl radicals ( $\text{HO}^\bullet$ ) [33]. The proposed pathway for  $\text{HO}^\bullet$  generation is presented in Equations 2 and 3 [3, 34].



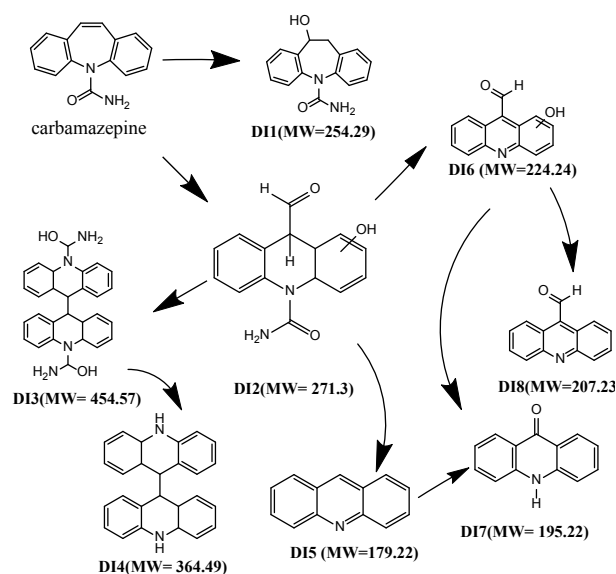
CBZ radicals may be generated by direct photolysis, and then the CBZ radical becomes able to oxidize water to generate  $\text{HO}^\bullet$  (Equation 2). Hydroxyl radicals then participate in CBZ hydroxylation.

In this study, the main intermediates of CBZ were monitored by LC/MS followed by detection via UPLC (Synapt G2-S HDMS in positive ion mode). To investigate the by-products formed by solar photo-degradation of CBZ in the CPC2 reactor, photo-transformation of CBZ (3 mg/L) was accomplished at a solar irradiation time of 3 h and initial pH value of 9. In Figure 6 a scan LC/MS analysis of CBZ intermediates is shown. CBZ photo-transformation intermediate molecular weights were assigned on the basis of the  $m/z$  quantity of the protonated molecule  $[\text{M} + \text{H}]^+$ . Generally, eight intermediates of CBZ were recognized. The proposed structures and pathways of the main photodegradation intermediates were shown in Figure 7. For simplification in this Figure and further, the detected intermediates (DI) are numbered from 1 to 8 in Figure 7.

CBZ photo-transformation under solar irradiation is likely to progress with photoionization (facilitated by dissolved oxygen to generate the radical cation of CBZ) and hydration of the double bond on the central heterocyclic ring of CBZ [34]. The potential structures of reaction products were tentatively proposed based on the accurate masses and similar studies [34-37]. Hence, an extensive description of MS data analysis is not provided here. Hydration of the double bond on the central heterocyclic ring is a minor route leading to 10, 11-Dihydro-10-Hydroxy Carbamazepine ( $\text{DI}_1$ ). This hydration can occur in the



**Figure 6:** Scan LC/MS analysis of CBZ intermediates in the CPC<sub>2</sub> (initial CBZ concentration 3 mg/L, the solar irradiation time of 3 h and initial pH value of 9).



**Figure 7:** The proposed structures and pathways of the main photo-transformation detected intermediates (DI) (based on LC/MS scan of CBZ intermediates and Chiron et al. [34]).

absence of light at near-neutral pH [34]. The photo ring expansion reaction was suggested to be the main pathway for the other detected intermediates ( $\text{DI}_2$  -  $\text{DI}_8$ ) [38]. A photo ring expansion reaction likely participates in the formation of carbamazepine-9-carboxaldehyde ( $\text{DI}_2$ ) resulting from a hydroxylation. Complementary hydroxylation of  $\text{DI}_2$  with loss of the side chain ( $\text{CH}_2\text{NO}$ ) yielding hydroxyacridine-9-carboxaldehyde ( $\text{DI}_6$ ), Acridone ( $\text{DI}_7$ ) and Acridine-9-carbaldehyde ( $\text{DI}_8$ ). The concurrent loss of the carboxyaldehyde group and the side chain ( $\text{CONH}_2$ ) leads to  $\text{DI}_5$  (acridine). Also, Acridine ( $\text{DI}_5$ ) oxidation can yield Acridone ( $\text{DI}_7$ ).

$\text{DI}_2$  (carbamazepine-9-carboxaldehyde) dimerization and reduction of the CHO side chain lead to  $\text{DI}_3$  and more reduction of the CHON side chain of  $\text{DI}_3$ , yielding

DI4[34]. According to this analysis of CBZ transformation by-products, it seems that complete mineralization of drug did not occur. However, the use of a CPC reactor equipped with a tracking system had a significant effect on the photo-transformation of CBZ.

## 4 Conclusions

Solar degradation and the effectiveness of CPC equipped with a sun tracker were examined using three different reactors: tube reactor (blank), CPC<sub>1</sub> and CPC<sub>2</sub>. According to the results, neither experimental reactor was completely effective alone, but the use of a CPC reactor equipped with a tracking system has a significant effect on CBZ degradation. The results also showed that increasing the reactor temperature with a copper rod (CPC2) did not significantly change CBZ degradation efficiency. Therefore, it seems likely that the role of temperature is less important than solar irradiation in CBZ degradation. It seems that the drug complete mineralization did not occur in these reactors. However, the use of a CPC reactor equipped with a tracking system has a significant synergistic effect on the photo-transformation of CBZ. It would be of importance to investigate the efficiency of this technique on solar photocatalytic degradation of water and wastewater contaminants.

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**Conflict of interest:** Authors state no conflict of interest.

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