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Comparative Analysis of Photodegradation of Ibuprofen and Clotrimazole Water Pollutant Using UVC Rays in Presence and Absence of ZnO Photocatalyst †

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Abstract: The recent surge in pharmaceutical micro-pollutants in water bodies calls for an efficient method to neutralize wastewater to sustain the ecosystem. One of the ways to degrade drug molecules is through photocatalytic degradation using UV rays. ZnO is known to be a common catalyst in the degradation of contaminants found in wastewater. However, due to its toxicity to the environment, there is a need to objectively re-evaluate its necessity and alternatives. In addition, most studies have focused on the utilization of UVA/UVB rays for the photocatalytic degradation process, as such, there are currently limited studies evaluating the efficacy of UVC for such purpose. In this work, we provide a comparative analysis of the photodegradation of drug molecules using UVC rays with and without the ZnO catalyst. Ibuprofen (IBP) and clotrimazole were used for analysis. We found that the use of a ZnO catalyst did not always produce better results. In some cases, we found that IBP was degraded more without ZnO (up to 94.4%) than with the ZnO (1 g/L) (up to 86.6%) in 60 min. However, without ZnO, we observed secondary metabolite by-products of IBP that required a longer treatment period to fully degrade. The inferior degradation strength for treatment with ZnO could be explained by increasing turbidity from adding greater concentrations of ZnO, which decreased the UV transmission to the IBP solution. To support the results, an investigation of the photocatalytic degradation of clotrimazole (an antifungal) with varying concentrations of ZnO as a catalyst was also carried out. The optimum ZnO concentration was determined to be ~1000 ppm, above or under which the efficiency of the degradation suffered. Thus, the use of a ZnO catalyst requires strict dosage control. Such tight regulation is not required for the system using just UVC rays, but it requires a longer treatment time to completely degrade the drug molecules and their by-products.

Keywords: photodegradation; photocatalytic; wastewater treatment

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1. Introduction

The discovery of micro-pollutants in the environment is a major concern that has yet to be addressed clearly [1]. Among the predominant examples of emerging organic contaminants (EDCs) are pharmaceutical and personal care products (PPCPs) [2]. Pharmaceuticals can reach water bodies through industrial, domestic, urban, agricultural, and hospital disposal via sewage systems [3]. Although wastewater treatment plants (WWTPs) are able to neutralize up to approximately 95% of these pharmaceutical components, they still end up in the environment at low concentrations [4]. Furthermore, typically, only large facilities, such as industrial plants, have such wastewater treatment plants.

Studies have shown that the toxicological effects of pharmaceutical micro-pollutants remain even at low concentrations of nanograms or micrograms per liter [5]. The release of micro-pollutants into the environment is highly dangerous for the ecosystem, as it

poses health risks to humans and animals and is hazardous to the environment [6]. The rapidly growing population contributes to the increased demand for the production and consumption of such components [7]. This raises the frequency and probability of the improper disposal of pharmaceuticals and the treatment of effluents, which inevitably increases the likelihood of pharmaceutical components being found in the environment as micro-pollutants [8]. Unwanted pharmaceutical pollutants have been found in various water bodies, such as rivers, lakes, groundwater, wastewater treatment plant (WWTP) effluents, and drinking water [9].

In this work, we investigated the photocatalytic degradation effectiveness of UV treatments on drug-contaminated water. UV water treatment is one of the simplest and most readily available methods for various public constituents, from households to large hospital facilities. This photocatalytic degradation study was carried out and analyzed via UV–Vis spectroscopy. Ibuprofen (IBP) and clotrimazole (CTZ) were chosen as the drug molecules of interest.

IBP is the world's third most consumed drug, making it a leading pharmaceutical micro-pollutant, as shown by its high detection rate in water systems around the world [10]. Many studies have explored the use of ZnO and/or TiO2 as catalyst(s) in the photocatalytic degradation of various pharmaceutical micro-pollutants and have shown promising results. The catalysts are activated upon UV irradiation, and highly oxidizing species are generated and aid in the process of degrading ibuprofen to its intermediates [11]. Sabouni et al. demonstrated that 94.5% of ibuprofen was degraded when ZnO was used as a photocatalyst after 120 min of UVA radiation [12]. Similarly, Jallouli et al. reported that ibuprofen was below the detection limit after 30 min of photocatalysis with TiO_2 [13].

CTZ is among the top 10 PPCP compounds when ranked according to its persistence, risk, bioaccumulation, toxicity, and occurrence in various countries [14]. Despite this, the degradation of CTZ is not commonly discussed, and very little information can be found. CTZ has a high degree of persistence, with a half-life of around 60 days and low biodegradability [15]. Naturally, CTZ can be degraded by physicochemical processes in soils and water or by being digested and metabolized by organisms [16]. However, the digestion of clotrimazole in non-target organisms can cause harmful effects. CTZ poses adverse effects on marine environments, especially in algae.

Our work presented herein aimed to provide new insights into the dynamic photocatalytic degradation of IBP and CTZ in UVC using various concentrations of ZnO as a catalyst. The time-dependent degradation of IBP and CTZ was analyzed using an exponential model, from which the maximum degradation efficiency and degradation rate were obtained. A recommendation based on the results is given to those seeking to employ UV waste treatment at their facilities.

2. Materials and Methods

2.1. Sample Preparation

Ibuprofen (IBP) powder was obtained from crushing Proris© tablets. The stock solution of IBP was prepared by adding 1 g of IBP powder into 1 L of methanol and stirring until complete dissolution was achieved. A serial dilution with distilled water was carried out to obtain 0, 10, 20, and 40 ppm IBP solution to construct the standard calibration curve. For example, to make the 40 ppm IBP solution, 4 mL of the IBP stock solution was diluted with 96 mL of distilled water. The sample tested was a 40 ppm IBP solution. For samples containing zinc oxide (ZnO), the solution was dosed with 1 g/L ZnO microparticles (SmartLab, molecular weight 81.39 g/mol) and stirred using a magnetic stirrer at 800 RPM for 30 min prior to irradiation. CTZ solutions (60 ppm) were prepared using similar methods to those used for IBP. CTZ degradation in the presence of ZnO was carried out at ZnO concentrations of 0.5, 1, 1.5, and 2 g/L.

2.2. Experimental Setup

The IBP solution (40 ppm, 100 mL) was put in a 120 mL glass beaker (Figure 1a). A UVC lamp (7-watt) was immersed in the solution. The solution was constantly stirred at room temperature while being irradiated to prevent particles from sedimenting on the bottom of the beaker. The magnetic stirrer was set to 460 RPM throughout the irradiation time. Samples were taken every 15 min during the irradiation time using a clean glass pipette.

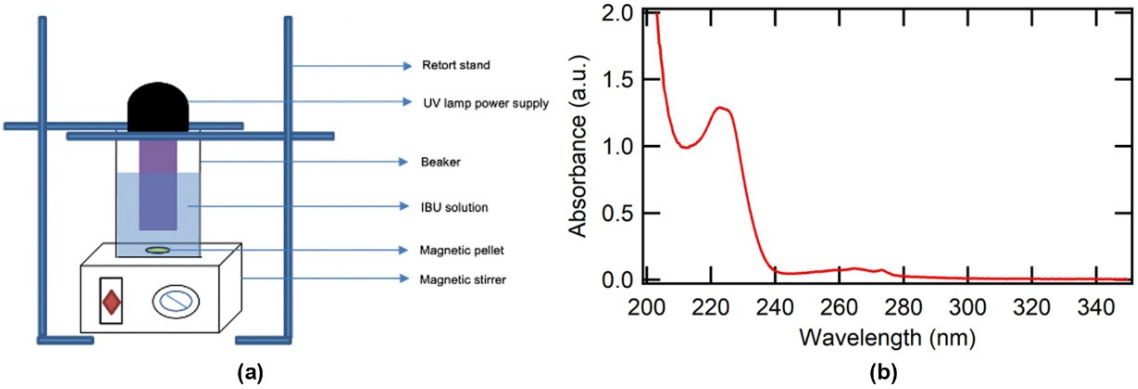

Figure 1. (**a**) Basic experimental setup and (**b**) basic UV–Vis profile of IBP.

2.3. Measurement and Analysis Using UV–Vis Spectrophotometer

UV spectra were obtained using a Jasco V730 UV–Vis Spectrophotometer in the UV region between 200 and 350 nm (Figure 1b). Generally, the main peak at 222.8 nm is considered the main IBP characteristic, whereas the profiles between 243 to 280 nm (represented by the peak at 273 nm) are accepted as characteristics of IBP intermediate degradation by-product molecules [17]. Peak height and background subtraction analysis were carried out using Spectra Manager. The IBP solution sample (40 ppm) was directly irradiated under constant stirring. Samples were taken at every 15-minute interval, and they were transferred into a quartz cuvette and put inside the UV–Vis Spectrophotometer to obtain the UV spectra. For samples containing ZnO, prior to obtaining the UV spectra, samples of IBP solution containing ZnO were first centrifuged for 10 min to separate the ZnO particles from the solution. The same method was applied to CTZ solutions but with peak wavelength observation at 263 nm [18].

3. Results and Discussion

3.1. Time Dependence of Degradation of IBP without and with ZnO Particles

The IBP solution was irradiated for 60 min, and the IBP concentration was analyzed every 15 min to investigate the degradation efficiency in terms of irradiation time (Figure 2). At around ~222 nm, which is the region for the main IBP peak, we observed the expected degradation of IBP upon UVC irradiation. In Figure 2a, we show the IBP concentration (C) decreased during the UV irradiation period with respect to the initial IBP concentration (C_0). A rapid decrease in the first 15 min is observed, and it followed an exponential trend for at least 60 min.

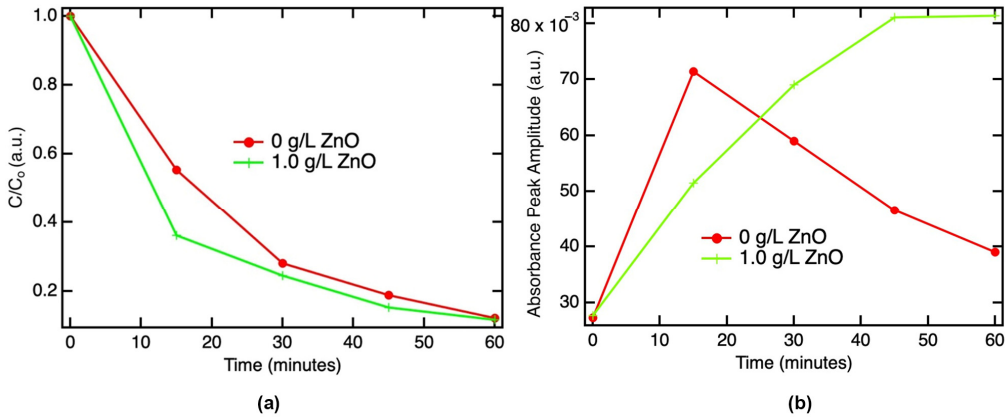

Figure 2. (**a**) IBP concentration (C/C_0) against irradiation time (minutes). The concentration of IBP was obtained by converting the absorbance peak amplitude of the IBP UV spectra at ~222 nm using a standard curve. (**b**) Absorbance (at 273 nm) of IBP by-product against irradiation time (minutes).

By contrast, a completely different situation was observed in the IBP by-product region around ~273 nm (Figure 2b). In the case of treatments without ZnO, we observed a clear formation of by-product molecules during the first interval, in which the most significant IBP degradation took place (Figure 2b). Subsequently, there was a continual decrease in the absorbance of the by-product molecules, which implied that it was also degraded alongside the IBP over the irradiation time. However, when ZnO was added, there was a distinct pattern of by-product formation that showed a gradual increase in absorbance accompanying the degradation of IBP. Unlike in the case of the absence of ZnO, the absorbance of by-products did not decrease over time, which means that the by-product was not degraded alongside the IBP. One possible by-product is 4-isobutylacetophenone, 4-IBAP, formed during the degradation of IBP under UV light [19]. 4-IBAP is known to be more toxic, and it takes longer to degrade than the parent compound, IBP [20].

3.2. Extraction of the Rate of IBP Degradation and Maximum IBP Degradation Potential

To further elucidate the performance characteristics of the UVC irradiation against IBP without and in the presence of ZnO, we applied an exponential model to time-dependent degradation curves shown in Figure 2a. The rate of degradation and maximum degradation potential were calculated with the following equation:

$$\frac{C}{C_0} = y_0 + e^{-kt}, \quad (1)$$

where C is the concentration, C_0 is the initial concentration, y_0 is the maximum degradation potential, k is the rate of degradation in min^{-1}, and t is irradiation time in min.

The extracted rate of degradation (k) and maximum degradation potential (y_0) are shown in Table 1. The rate of IBP degradation was greater in the presence of ZnO, which proves the photocatalytic abilities of ZnO. However, adding ZnO decreased the maximum degradation potential. This could be caused by the increase in turbidity and/or competition for adsorption sites on the surface of ZnO between the IBP and its by-product.

Table 1. k constant and maximum degradation potential of IBP.

ZnO Concentration (g/L)	k (min^{-1})	Maximum Degradation Potential (%)
0	0.045	94.4
1	0.083	86.6

Thus, adding ZnO as a photocatalyst is recommended in situations in which time is limited and the rate is prioritized over achieving the maximum degradation potential.

When time is not a constraint, UVC treatment in the absence of ZnO is recommended. This yielded the greatest maximum degradation potential of 94.4%, although at a slower rate. Another consideration is that UVC treatment in presence of ZnO left a considerably high amount of IBP remaining in the solution, which might still be toxic if released into the environment.

3.3. Clotrimazole Degradation Rate and Maximum Degradation Potential

Similar characterization and analysis were also carried out for the clotrimazole solution. In Table 2, we show the results of the extracted degradation rate (k) and maximum degradation potential (y_0). The value of k increased from 0–1.0 g/L of ZnO and reached a maximum at 1.0 g/L before decreasing when more ZnO was added. At the highest ZnO concentration of 2.0 g/L, k was lower than that of without ZnO, showing again how the excessive addition of ZnO is inefficient and might reverse its photocatalytic abilities. Similar to the degradation of IBP, high concentrations of ZnO increased the solution turbidity, which might limit light transmission and prevent the photolysis of CTZ, hence resulting in lower k values and degradation efficiency.

Table 2. k constant and maximum degradation potential of CTZ.

ZnO Concentration (g/L)	k (min^{-1})	Maximum Degradation Potential (%)
0	0.025	92.0
0.5	0.034	95.2
1.0	0.051	99.9
1.5	0.047	95.9
2.0	0.023	93.0

Overall, the degradation potential of CTZ in UVC showed good results, with over 90% of the maximum degradation potential at all concentrations of ZnO. The lowest potential was reached without ZnO at 92%, whereas the greatest potential was reached when 1.0 g/L of ZnO was added, at 99.9% or close to complete degradation. Again, exceeding this optimum concentration of ZnO decreased the degradation efficiency or the maximum degradation potential, with the lowest at 93% when 2.0 g/L of ZnO was added and an expected continual decrease with the increase of ZnO concentration owing to the increase in turbidity. In the case of CTZ, the greatest k value and maximum degradation potential were achieved when 1.0 g/L of ZnO was added, indicating that this is its optimum ZnO concentration.

It is worth noting that in the case of CTZ, we did not observe the presence of by-products in the UV spectra. Thus, there was likely to be no competition between the adsorption sites of the main drug molecules and their by-products, as was the case for IBP. This could explain why, in general, the addition of ZnO works better for CTZ than IBP.

4. Conclusions

Although it is generally perceived that the addition of ZnO as a photocatalyst increases the effectiveness of UV treatments for degrading pharmaceutical micro-pollutants, our work revealed that there are various outcomes that require careful investigation. We found that IBP was not as efficiently degraded when ZnO was used in the solution during the UVC treatment (the maximum degradation potential was 86.6%) as it was without ZnO (94.4%). Despite the ability of ZnO to degrade the IBP faster, this advantage was superseded by its inability to degrade the IBP by-product. In other cases, such as that of CTZ, a high degradation efficiency with and without ZnO was observed. The use of ZnO for degrading CTZ appears to be better than that without, with maximum degradation potentials of 99.9% and 92%, respectively. The optimal ZnO concentration was determined to be ~1 g/L, above which screening effects due to increased turbidity started to dominate the system, which lowered the photodegradation effectiveness. Overall, it is clear that UVC without ZnO was sufficiently effective in degrading IBP and CTZ, with a maximum degradation potential

of more than 90% in both cases. Furthermore, the by-product of IBP was also shown to be more effectively degraded without ZnO. Thus, we hope that our results may further encourage the adoption of a simple UVC batch-stirred treatment system to treat wastewater in households, hospitals, and the pharmaceutical industry.

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