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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: 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 are focused on 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 photodegradation of drug molecules using UVC ray with and without the ZnO catalyst. Ibuprofen (IBP) and clotrimazole are used for analysis. We found that the use of ZnO catalyst does not always produce better results. In some case, we found that IBP was degraded up to 94.4% more than that 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 require longer treatment period to fully degrade. The inferior degradation strength for treatment with ZnO can be explained by increasing turbidity from adding greater concentrations of ZnO which decreases the UV transmission to the IBP solution. To support the results, an investigation on the photocatalytic degradation of clotrimazole, an antifungal, with varying concentrations of ZnO as catalyst was also carried out. The optimum ZnO concentration was determined to be ~1000 ppm, above or under which the efficiency of the degradation suffers. Thus, the use of ZnO catalyst require strict dosage control. Such tight regulation is not required for the system using just UVC ray, but it would require a longer treatment time to completely degrade drug molecules and its by-products.

Keywords: photodegradation; photocatalytic; wastewater treatment

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1. Introduction

The discovery of micro-pollutants in the environment has been a major concern that is yet to be addressed clearly [1]. One of the predominant examples of emerging organic contaminants (EDCs) is 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 the wastewater treatment plant (WWTP) is able to neutralize up to approximately 95% of these pharmaceutical components, it still ends 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-pollutant remain even at low concentrations of nanograms or micrograms per liter [5]. The release

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

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

IBP is the world's third most consumable drug, consequently making it a dominating pharmaceutical micro-pollutant 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 aids in the process of ibuprofen degradation to its intermediates [11]. Sabouni et al. has demonstrated 94.5% of ibuprofen degradation using ZnO as a photocatalyst after 120 min of UVA radiation [12]. Similarly, Jallouli et al. has reported that ibuprofen was below the detection limit after 30 minutes 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 a low biodegradability [15]. Naturally, CTZ can be degraded by physicochemical processes in soils and water, or by being disgested 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 algae.

Our work presented herein aims to provide new insights to the dynamic photocatalytic degradation of IBP and CTZ in UVC using various concentrations of ZnO as catalyst. Time-dependent degradation of IBP and CTZ were analyzed using an exponential model from which the maximum degradation efficiency and degradation rate are obtained. Based on the results, a recommendation 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. A serial dilution with distilled water was carried out to obtain 0, 10, 20, and 40 ppm IBP solution for obtaining the standard calibration curve. For example, to make the 40 ppm IBP solution, 4 mL of the IBP stock solution is diluted with 96 mL of distilled water. The sample under test was 40 ppm IBP solution. For samples containing zinc oxide (ZnO), the solution was dosed with 1 g/L of ZnO microparticle (SmartLab, molecular weight 81.39 g/mol) and stirred using a magnetic stirrer at 800 RPM for 30 minutes prior to irradiation. CTZ solutions (60 ppm) were prepared using similar methods as that of the IBP. CTZ degradation in the presence of ZnO was carried out at ZnO concentrations of 0.5, 1, 1.5, 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 into the solution. The solution is constantly stirred at room temperatures while being irradiated to prevent particles from sedimenting on the bottom of the beaker. The magnetic stirrer is set to 460 RPM throughout the irradiation time. Samples were taken every 15 minutes interval of irradiation time using a clean glass pipette.

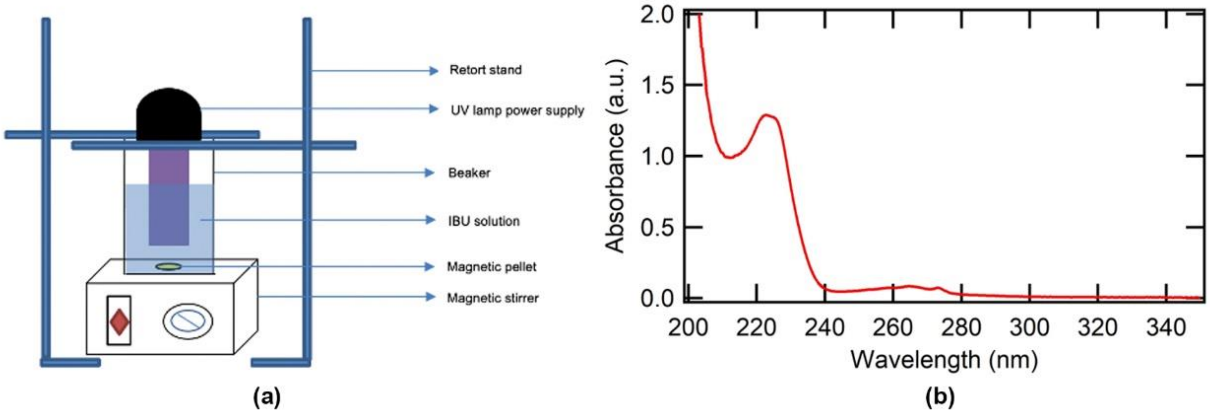

Figure 1. (**a**) Basic experimental setup and (**b**) basic UV-Vis profile of IBP.

2.3. Measurement and Analysis Using UV-Vis Spectrophotometer

UV spectra were obtained using 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 as the main IBP characteristic, whereas the profiles between the 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 where 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 minutes to separate the ZnO particles from the solution. The same method applies to CTZ solutions but with peak wavelength observation at 263 nm [18].

3. Results & Discussion

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

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). 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) decrease upon UV irradiation period with respect to the initial IBP concentration (C_o). A rapid decrease in the first 15 min is observed and follows an exponential behavior up until at least 60 min duration.

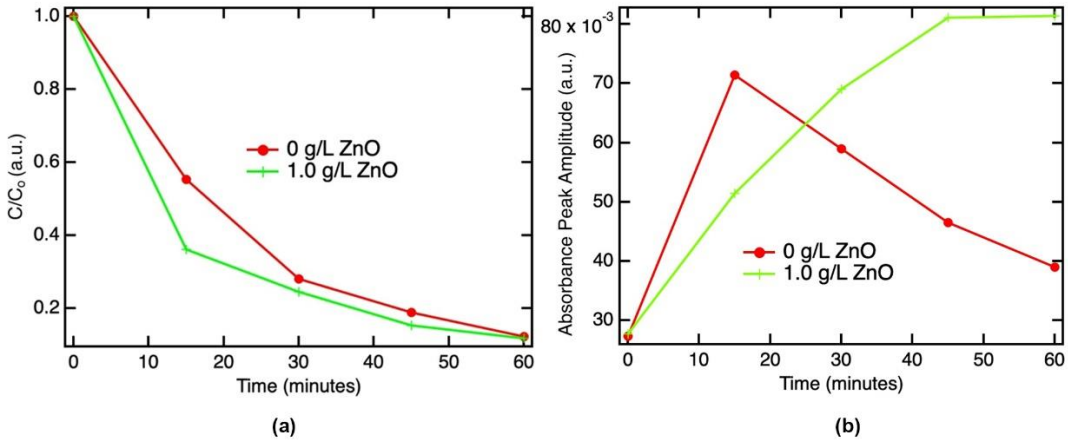

Figure 2. (**a**) IBP concentration (C/C_0) against irradiation time (minutes). The concentration of IBP was obtained by converting the absorbance peak amplitude of the IBP UV spectra at ~222 nm using a standard curve. (**b**) Absorbance (at 273 nm) of IBP by-product against irradiation time (minutes).

In 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 where the most significant IBP degradation takes place (Figure 2b). Subsequently, there is a continual decrease in the absorbance of the by-product molecules, which implies that it is also degraded alongside the IBP over irradiation time. However, when ZnO is added, there is a distinct pattern of by-product formation that shows a gradual increase in absorbance accompanying the degradation of IBP. Unlike in the case of the absence of ZnO, the absorbance of by-products does not decrease over time, which means that the by-product is 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 presence of ZnO, we apply an exponential model to time-dependent degradation curves shown in Figure 2a. The rate of degradation and maximum degradation potential are calculated with the following equation:

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

where, C is the concentration, C_o 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 the rate of degradation (k) and maximum degradation potential (y_0) are shown in Table 1. The rate of IBP degradation is greater in the presence of ZnO, which proves the photocatalytic abilities of ZnO. However, adding ZnO decreases 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 photocatalyst is recommended in situations where time is limited and rate is prioritized over achieving the maximum degradation potential. When time is not a constraint, the UVC treatment in the absence of ZnO is recommended. It yields the greatest maximum degradation potential of 94.4% although at a slower rate. Another consideration is that UVC treatment in presence of ZnO leaves a considerably high amount of IBP remaining in the solution, which might still be toxic if released to the environment.

3.3. Clotrimazole Degradation Rate and Maximum Degradation Potential

Similar characterization and analysis were also carried out for 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 increases from 0–1.0 g/L of ZnO and reaches a maximum at 1.0 g/L before decreasing when more ZnO is added. At the highest ZnO concentration of 2.0 g/L, k is 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 increases solution turbidity that 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 UV-C shows good results with over 90% of maximum degradation potential in all concentrations of ZnO. The lowest potential is reached without ZnO at 92%, whereas the greatest potential is reached when 1.0 g/L of ZnO is added at 99.9% or close to a complete degradation. Again, exceeding this optimum concentration of ZnO decreases the degradation efficiency or the maximum degradation potential with the lowest at 93% when 2.0 g/L of ZnO is 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 are achieved when 1.0 g/L of ZnO is 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-product in the UV spectra. Thus, there is likely to be no competition of adsorption sites between the main drug molecules with its by-products as in the case of IBP. This could explain why in general the additional of ZnO works better in CTZ compared to that in IBP.

4. Conclusions

Although it was generally perceived that the addition of ZnO as photocatalyst increases the effectiveness of UV treatments for degrading pharmaceutical micro-pollutants, our work reveals that there are various outcomes that require a careful look. We found that IBP was not as efficiently degraded when ZnO was used in the solution during the UVC treatment with maximum degradation potential of 86.6% compared to that without ZnO at 94.4%. Despite the ability of ZnO to degrade the IBP faster, this advantage is superseded by its inability to degrade the IBP by-product. In other case such as in CTZ, high degradation efficiency with and without ZnO are observed. The use of ZnO for degrading CTZ appears to be better than that without with maximum degradation potential of 99.9%

and 92%, respectively. Optimal ZnO concentration was determined to be ~1 g/L, above which, screening effects due to an increased turbidity starts to dominate the system which lowers the photodegradation effectiveness. Overall, it is clear that UVC without ZnO is 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 is 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 pharmaceutical industries.

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