Reaffirming the Critical Role of Transformative Research and Knowledge Production in the Age of Post-Truth

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Determination of Efficiency of Trimethoprim Degradation Under UV and Persulfate Systems

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Abstract: Trimethoprim (TMP) as an aquatic pollutant poses ecological and human health-related risks as the antibiotic is highly soluble in water, resistant to biodegradation, and induces moderate chronic toxicity. Its prolonged presence in the environment resulted in certain bacteria strains developing antibiotic resistance. Since there is currently a relatively high wastewater residual concentration of the antibiotic, traditional wastewater treatment methods are ineffective at getting rid of it. Thus, a viable method for the removal of TMP is through Advanced Oxidation Processes (AOPs), which utilize radicals such as sulfate radicals to react with organic pollutants. As part of the study, the degradation efficiency of TMP under UV, $S_2O_8^{2-}$, and UV/$S_2O_8^{2-}$ systems was determined through UV-vis spectrophotometry. It was found that the joint UV/$S_2O_8^{2-}$ system degraded TMP at a relatively higher rate, averaging at a degradation efficiency of 38.61%. Moreover, the system reached a peak degradation of 53.21% during the first trial. Conversely, it was found that the UV and $S_2O_8^{2-}$ systems did not show reliable and significant degradation resulting in average degradation efficiencies of 4.53% and -3.17%, respectively. Determining viable methods of degrading TMP in wastewater could benefit wastewater treatment facilities and the academic community and show improvements in global health quality.

Keywords: Trimethoprim; ultraviolet (UV); photodegradation; degradation efficiency; persulfate

1. INTRODUCTION

1.1. Background of the Study

Industrial endeavors have generated an array of biological and chemical pollutants in marine environments, including but not limited to heavy metals, industrial pollutants, agricultural contaminants, and pharmaceuticals (Kisala et al., 2021; Shahid, 2021; United Nations Environment Programme, 2021). Among these, the presence of pharmaceuticals is of primary concern due to the projected increase in the volume of antibiotic consumption in the following years. According to Van Boeckel et al. (2017), the global antibiotic usage for livestock alone is forecasted to reach 200,325 tons in 2030. Moreover, pharmaceuticals are considered to be an expanding category of Persistent Organic Pollutants (POPs) (Ayankojo et al., 2022). Aravind Kumar et al. (2022) defined POPs as pervasive organic compounds that survive in the environment over prolonged durations due to resistance to biodegradation, bioaccumulation, and toxicity despite their presence in lower concentrations.

Among these antibiotics, Trimethoprim (TMP), predominantly used in treating urinary tract infections, pneumonia, and more, is the 2nd most highly consumed antibiotic, with around 3.62 billion capsules consumed in 2015 (American Society of Health-System Pharmacists, 2022; Bortone et al., 2021). However, the liver only processes 10–20% of a TMP dose. As a result, roughly 80% of the unmodified medication is retrieved in urine and is eventually exposed to aquatic biodiversity. In such settings, TMP has a minimal potential for bioaccumulation, a moderate chronic toxicity, as well as the potential to persist (Health and Medical Care Administration, 2021). The Minnesota Department of Health (2015) has also classified TMP as a Contaminant of Emerging Concern for its persistence in the environment. Moreover, due to the development of certain genes, bacteria that are resistant to antibiotics have emerged

as a result of the presence of TMP in the environment, particularly in aquatic ecologies (Wang et al., 2019). Since the wastewater residual concentration of the antibiotic ranges from 0.1 to 5 µg/L, traditional wastewater treatment methods, such as filtration, coagulation, and more, are ineffective at getting rid of it (Yang et al., 2020).

As a result, Advanced Oxidation Processes (AOPs) have been utilized in the degradation of organic pollutants, such as TMP. AOPs oxidize organic substances through interactions with radicals that react rapidly (Glaze et al., 1987). Go (2020) utilized AOPs for the degradation of levofloxacin, an antibiotic known to cause chronic toxic effects to marine organisms, and was able to achieve a degradation efficiency of 70.6%. Sulfate-Radical-Based AOPs, commonly activated through UV radiation, have lately grown in prominence due to their effectiveness in treating wastewater contaminants like antibiotics and other organic pollutants (Xia et al., 2020). Sulfate radicals outperform the frequently utilized hydroxyl radicals in terms of redox potential, reactional pH condition, half-life, and oxidation capacity (Li et al., 2019). Furthermore, in addition to eliminating harmful pollutants, this process can also reduce the toxicity of their products.

1.2. Research Objective

Due to the lack of information regarding the degradation of TMP using Sulfate-Radical-Based AOPs in the current body of knowledge, the purpose of this study is to determine the efficiency of TMP degradation. Specifically, this research would identify the peak absorbance of TMP. A calibration curve would then be created to correlate absorbance and concentration. Lastly, the degradation efficiency of a UV-illuminated system, an unlit $S_2O_8^{2-}$ system, and a UV/$S_2O_8^{2-}$ system will be compared.

1.3. Scope and Limitations

In the study, UV-Vis spectroscopy was performed to measure peak absorbance (λmax). A calibration curve was constructed to convert the measured absorbance at λmax directly to TMP concentration by extrapolation and determine the residual concentrations of TMP (Wuana et al., 2015). Using the data obtained from the calibration curve, the efficiency of the degradation of TMP under a UV-illuminated system, an unlit $S_2O_8^{2-}$ system, and a UV/$S_2O_8^{2-}$ system were compared. As this paper tested different systems, the most and least efficient systems were identified.

1.4. Significance of the Study

This study will present additional findings to the scientific community, the aquatic-affiliated critical infrastructure sector, and the world (Cybersecurity and Infrastructure Security Agency, n.d.). The research findings would supplement the existing body of knowledge regarding the photodegradation of TMP under UV irradiation. The conclusions formed would aid the water and wastewater systems sector in innovating efficient and ecological methodologies aimed at mitigating emerging marine pollutants. Lastly, the world would benefit from the data collected as it is concerned with marine ecosystems and human health quality.

2. METHODOLOGY

2.1 Material Procurement

Throughout the experiment, the following materials were used: Trimethoprim ($C_{14}H_{18}N_4O_3$) high-performance liquid chromatography (HPLC) grade ≥ 99.0%, Potassium Persulfate ($K_2S_2O_8$), and American Chemical Society (ACS) grade reagent ≥ 99.0%. These materials were purchased from Sigma-Aldrich. Methanol (MeOH) was also used and was obtained from the De La Salle University Chemistry Department Laboratory.

2.2. Research Design

The study was quantitative in nature, which enabled the researchers to fulfill the research objectives using numerical observations and calculations.

The study presented two ethical issues. Firstly, the treatment and handling of laboratory-grade chemicals. Thus, the researchers attended a laboratory seminar to prevent the mishandling of the substances to be utilized. Secondly, numerical data retrieved using various laboratory techniques were raw. Data collection possessed the possibility of personal errors. As such, to reduce errors and inaccuracy, multiple trials were conducted.

2.3 Data Collection Method

Using the UV-Vis spectrophotometer, TMP was analyzed to determine its peak absorbance. Using the same instrument, the calibration curve was determined using nine TMP solutions. Each of the solutions had different concentrations of TMP: 100mL of 0 ppm, 0.5 ppm, 1 ppm, 3 ppm, 5 ppm, 7 ppm, 10 ppm, 15 ppm, and 20 ppm. The corresponding absorbance values obtained were used to match the absorbance values of the degraded TMP solutions to determine the concentration of TMP in each system.

In set-up 1, TMP was degraded via UV radiation, with 100 mL of 10 ppm TMP added to a 250 mL jacketed beaker. The beaker was magnetically stirred in the absence of electromagnetic radiation for 30 minutes at 600 rpm at room temperature, then stirred for two hours under UV light(20 W; λmax = 254 nm). In set-up 2, TMP was degraded with a $S_2O_8^{2-}$ system under dark conditions, with 100 mL of 10 ppm TMP and 200 ppm of $K_2S_2O_8$ added to a 250 mL jacketed beaker. The beaker was magnetically stirred continuously for 2.5 hours at 600 rpm under dark conditions at room temperature. In set-up 3, TMP was degraded using a UV/$S_2O_8^{2-}$ system, with 100 mL of 10 ppm TMP and 200 ppm of $K_2S_2O_8$ added to a 250 mL jacketed beaker. The beaker was magnetically stirred in the absence of electromagnetic radiation for 30 minutes at 600 rpm at room temperature, then stirred for two hours under UV light(20 W; λmax = 254 nm).

Throughout the experiment, at 15-minute intervals, 4 mL aliquots were taken from the three set-ups and transferred to test tubes filled with 2 mL of MeOH. The MeOH was placed to stop any further formation of free radicals, thereby allowing the researchers to determine the amount of degradation that occurred for a given time interval. The absorbance of TMP left undegraded was numerically characterized through a peak absorbance of 270 nm via UV-Vis spectroscopy.

The data from the UV-Vis spectrophotometer was analyzed using the calibration curve to determine the concentration values.

2.4 Data Analysis

The efficiency of degradation was determined by dividing the difference between the initial concentration (C_0) and the final concentration (C) by the initial concentration and expressing it in percentage. The degradation efficiency was then compared among the three systems.

$$\%\text{Degradation Efficiency} = [(C_0 - C)/C_0] \times 100\%$$

3. RESULTS AND DISCUSSION

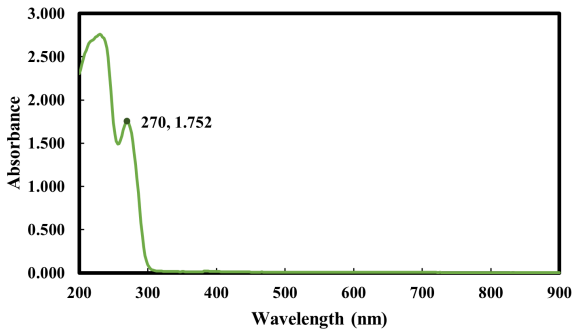
3.1. Peak Absorbance of TMP

The results obtained from the analysis of TMP using UV-vis spectroscopy revealed a distinct peak at a wavelength of 230 nm, as shown in Figure 3.1. According to Ji et al. (2016), the absorption of water is at a wavelength of around 200 to 245 nm. Therefore, this peak was not considered in the determination of TMP's peak absorbance since this peak would pertain to the peak absorbance of water.

Moreover, a second distinct peak at a wavelength of 270 nm with an absorbance of 1.752 was identified. This finding suggests that TMP exhibits a high degree of absorption at this particular wavelength. Therefore, this wavelength would be utilized in subsequent analysis of the degradation of TMP.

Figure 3.1

Peak Absorbance Graph



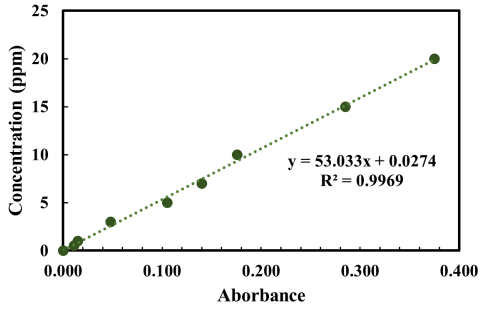
3.2. Calibration Curve

The calibration curve derived from the experimental data, as depicted in Figure 3.2, demonstrates a highly linear relationship between the absorbance (x) and the concentration of TMP in parts per million (ppm) (y). The

obtained linear model exhibits an R-squared (R^2) value of 0.9969, indicating relatively precise measurements. The equation y = 53.033x + 0.0274 was determined to directly convert absorbance readings into TMP concentration values.

Figure 3.2

Calibration Curve

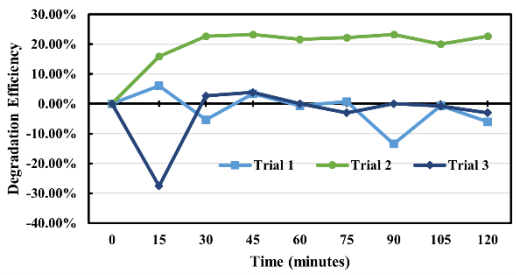


3.3. Degradation of TMP

The effectiveness of UV by itself as a treatment method for the degradation of TMP in aqueous solution was assessed. In the system containing only persulfate and the TMP solution, as seen in Figure 3.3.1, after the 30-minute mark, no remarkable changes were observed. The degradation of TMP using the UV system showed inconsistent results. Trials 1 and 3 showed that UV was not effective at degrading TMP with a degradation efficiency of -6.06% and -3.02 respectively, while trial 2 showed an increase in degradation efficiency of 22.69%. Similar to the system with only persulfate, the inconsistency in the degradation efficiency of the trials signifies that UV alone is not effective at degrading TMP. The direct UV photolysis of TMP was slower due to the antibiotic's quantum yield being less than one and low molar absorptivity at 254 nm (Luo et al., 2021).

Figure 3.3.1

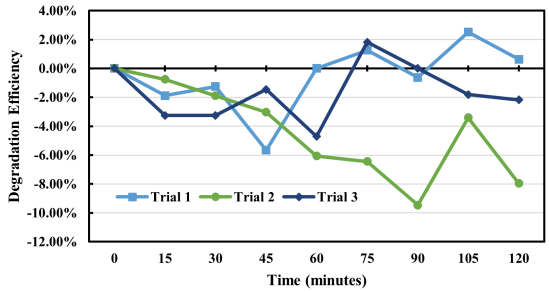
UV System



Secondly, the effectiveness of persulfate by itself as a treatment method for the degradation of TMP in an aqueous solution was assessed. In the system containing only persulfate and the TMP solution, as seen in Figure 3.3.2, all three trials showed consistent concentration values, with degradation efficiency ranging from 4.00% to -10.00% of degradation. As such, the results suggest that persulfate alone may not significantly contribute to the reduction of TMP concentration. The innate characteristics of persulfate as an oxidant may be the cause of its observed low degradation effectiveness (Gao et al., 2022). It has been noted that without additional catalytic or modifying agents such as ultraviolet light, persulfate is less effective at degrading some types of pollutants.

Figure 3.3.2

Persulfate System

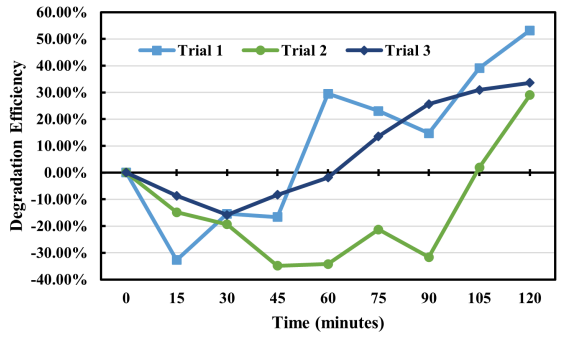


Lastly, the effectiveness of UV and persulfate used in conjunction for the degradation of TMP was then examined. This system showed a significantly higher degradation, with 53.03%, 28.94%, and 33.58% final degradation efficiency for the three trials. However, as shown in Figure 3.3.3, an unexpected increase in TMP concentration

was observed from the 0 to 60-minute interval of UV exposure, resulting in a negative degradation efficiency. Given this, it is hypothesized that the increase in concentration resulted from the presence of degradation products which then also degraded as the process continued.

Figure 3.3.3

UV/Persulfate System



The results obtained from the study, as presented in Table 1, provide valuable insights into the efficiency of different systems in degrading TMP. Notably, the systems that solely relied on either UV or persulfate exhibited limited degradation of TMP, with average degradation efficiencies of 4.53% and -3.71%, respectively. However, a significant improvement in the degradation efficiency was observed when both UV and persulfate were combined synergistically. The system that utilized both UV and persulfate in conjunction with one another exhibited an average degradation efficiency of 38.61%. These results indicate that the UV/$S_2O_8^{2-}$ system has a substantially higher potential for TMP degradation compared to the individual UV or persulfate systems. The interaction between UV and persulfate promotes the generation of sulfate radicals which are highly reactive and capable of efficiently degrading TMP molecules. Therefore, these results highlight the potential of UV and $S_2O_8^{2-}$ as a promising approach for the degradation of TMP in aquatic environments.

Table 1

Degradation Efficiency

Trial Number	Systems		
	UV	Persulfate	UV/ Persulfate
1	-6.06%	0.63%	53.21%
2	22.69%	-7.95%	29.03%
3	-3.02%	-2.17%	33.58%
Average	4.53%	-3.17%	38.61%

4. CONCLUSIONS

This study has investigated the TMP degradation efficiency of three systems: unlit $S_2O_8^{2-}$ system, UV system, and UV/$S_2O_8^{2-}$ system. It was concluded that the combined UV/$S_2O_8^{2-}$ system degraded TMP in the aqueous solution at a relatively higher rate, averaging at a degradation efficiency of 38.61%. Furthermore, the mentioned system reached a peak degradation of 53.21% during the first trial.

To improve the study, however, it is recommended to further analyze the samples via Liquid Chromatography Mass-Spectrometry Quadrupole Time of Flight (LC-MS QToF) to verify the presence of degradation products and the cause of unexpected spikes in absorbance during trials. Moreover, it is also recommended to determine the toxicity of determined byproducts using the Ecological Structure Activity Relationships (ECOSAR) software.

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