Effects on sulfur mustard degradation when lighting conditions are changed

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Introduction

One of the biggest threats against the safety of a solider is chemical warfare. There are many chemical warfare agents (CWAs) that can be used against a solider. One of the most horrific CWAs is sulfur mustard, also known as mustard gas. Mustard gas is highly reactive with water and forms hydrochloric acid. When this acid touches human skin, chemical burns are almost immediately observed. Inhalation leads to the most lethal aspect of the gas. The reaction will occur in the throat and lungs, creating burns and asphyxiation. There is a way to break down this gas in the form of a photocatalytic reaction. Mustard gas, when exposed to light and a catalyst, will break down into a non-toxic material known as dichlorodiethyl sulfoxide (Wang et al., 2018). The goal of this project was to optimize the distance of the light from the mustard gas and catalyst to most effectively break down the gas into the non-toxic substance.

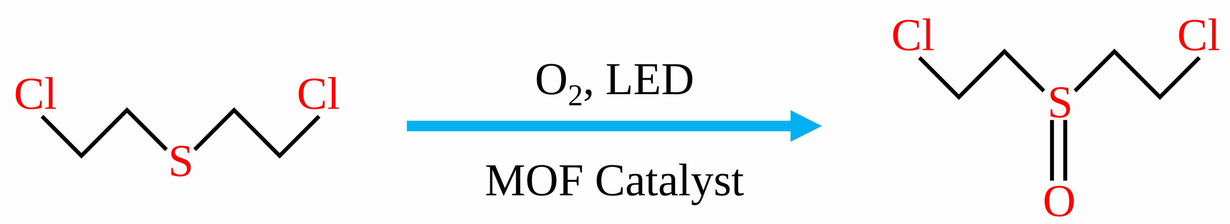


Figure 1 (above): A model of how sulfur mustard is degraded

Figure 1 shows this process of the oxygen attaching, known as photooxidation. Through this reaction, the compound breaks down into a substance that no longer reacts to create harmful byproducts such as hydrochloric acid. Singlet oxygen is believed to be the reactant species. The purpose of this experiment was to find the optimal distance from which a light could be shined on a mixture of Metal Organic Framework (MOF) catalyst and an imitation compound for mustard gas, known as methylene blue, to have the most efficient rate of decay.

Materials and Methods

The purpose of this project was achieved through an adjustable LED light emitting UV radiation (Figures 2 and 3) pointed at the MOF catalyst (NU-1000) and methylene blue. The light was moved varying distance (5 cm, 7.5 cm, 10 cm, and 15 cm) away from the reaction and data was taken at time points 2, 4, 6, 8, and 10 minutes. At each of these time points, the vial with the mixture was removed and placed into a device called a UV-vis spectrometer. This machine sent visible light through the mixture and could measure the absorbance of the light by the methylene

Materials and Methods (cont.)

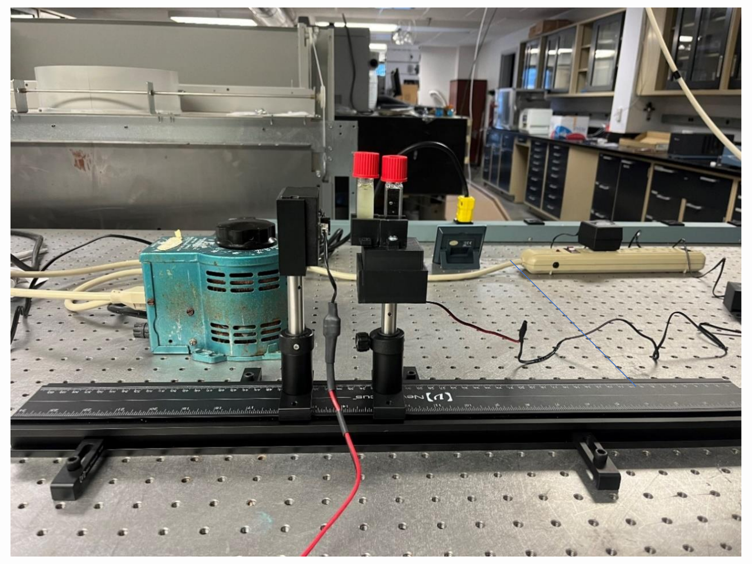


Figure 2 (above): A picture of the experimental setup before a test was run

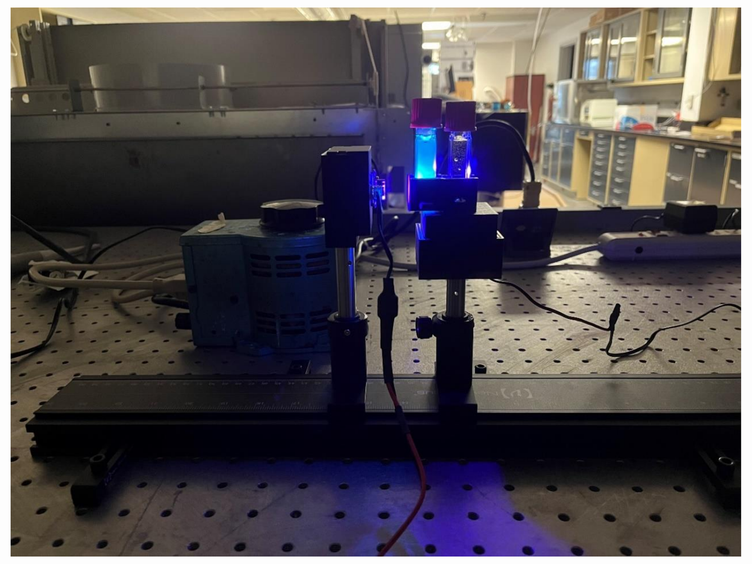


Figure 3 (above): A picture of the setup running an experiment

blue. Using this information, the remaining concentration could be quantified.

In this experiment, a science called actinometry was used. Actinometry is a study of the interaction between light and a substance. Due to the unknown rate of degradation for methylene blue, potassium ferrioxalate (Figure 4), with a known rate of degradation was used (Graph 2). This allowed for the calculation of the number of photons hitting the solution for a particular distance.

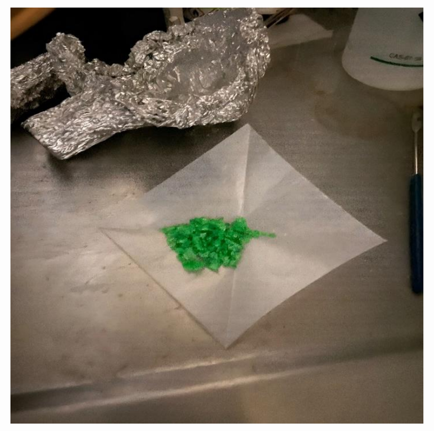


Figure 4 (left): A picture of the potassium ferrioxalate. This was used in the actinometry experiments. It gives off a set amount of iron that can be used to calculate the number of photons hitting the reaction at a particular distance. The reaction that the ferrioxalate undergoes is shown below (hυ is shorthand for light):

$$2[Fe(C_2O_4)_3]^{3-} + h\upsilon \longrightarrow 2Fe(C_2O_4) + 3[C_2O_4]^{2-} + 2CO_{2a}$$

Results

A line of best fit was made for the plot of methylene blue concentration versus time and a rate of degradation in each set of data was found (Table 1).

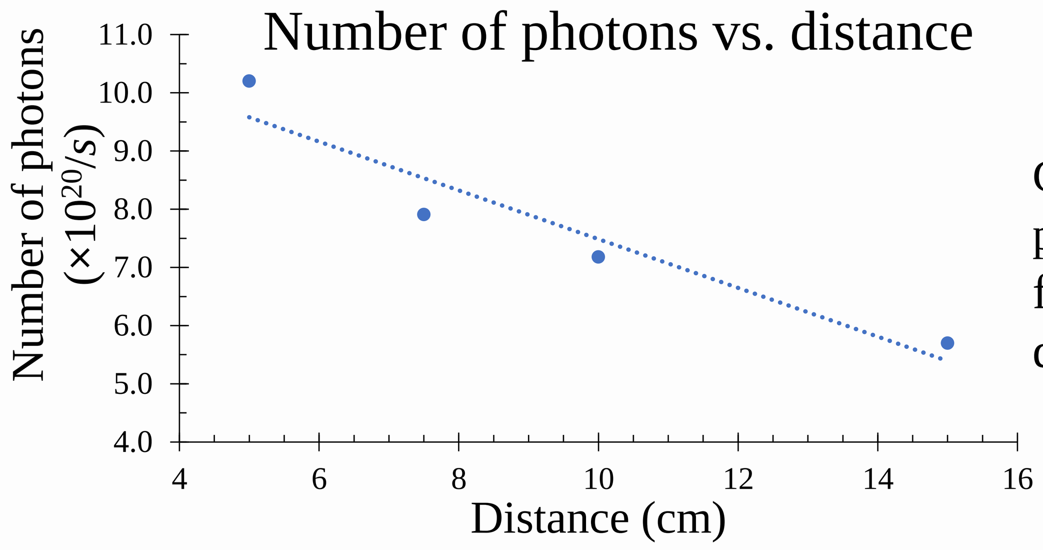
Table 1: The 15 cm data is not reported as it was essentially identical to the 10 cm data. With all R^2 values greater than .95, all data was considered valid.

Distance	Line of best fit equation	R^2 value
5 cm	$y = -7 \times 10^{-8}x + 5 \times 10^{-6}$	.998
7.5 cm	$y = -5 \times 10^{-8}x + 5 \times 10^{-6}$	.972
10 cm	$y = -3 \times 10^{-8}x + 5 \times 10^{-6}$	.966

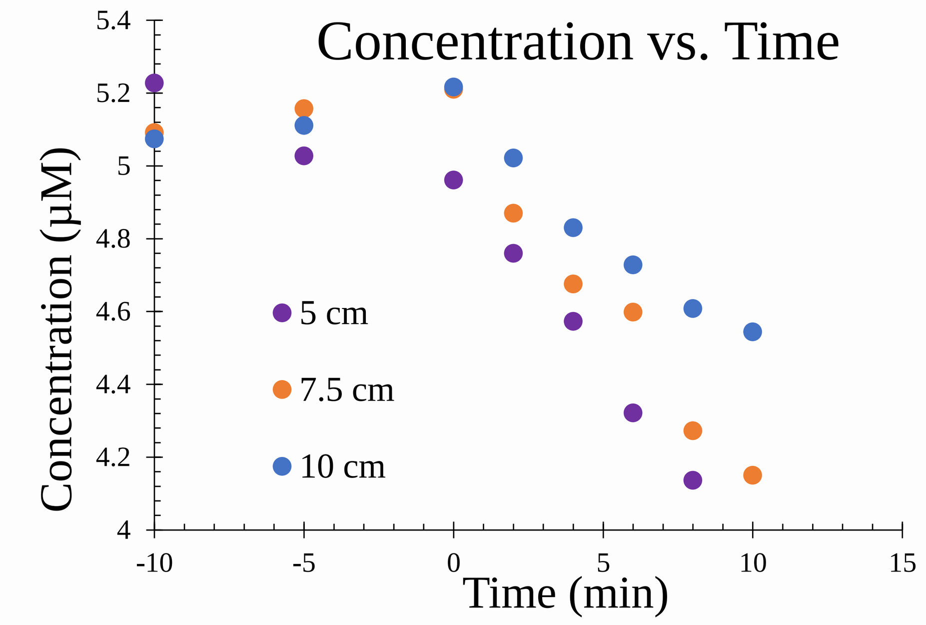
The 5 cm test showed the fastest rate of degradation, as that sample was hit by the largest number of photons (Graph 1). Graph 2 shows the degradation over time of the methylene blue and MOF mixture. At 5 cm, the concentration of the mixture was decreasing at the fastest rate, corresponding to the photon count findings. At 15 cm, the rate of degradation decreased to a point at which it was

Results (cont.)

no longer meaningful, as the photocatalysis was no longer happening at a significant rate.



Graph 1 (left): Number of photons hitting the potassium ferrioxalate at varying distances.



Graph 2 (left): Photocatalysis data at each distance from the light. Negative timepoints indicate time spent while the reaction was balancing and coming to a point where the methylene blue had fully been incorporated into the MOF.

Conclusions

As shown above, at 5 cm, the rate of degradation was highest. While in this experiment, the closest distance showed the fastest rate, the fastest rate occurs where the photon count is highest. Other studies such as one performed on DON (a toxin in grain) support a theory of an optimal distance (He P et al., 2018). This is where the rate of degradation is not fastest at the closest point but at where photon density is the highest. There are many variations of this test that can be performed. Different wavelengths of light and the number of lights are variables that could be changed in future studies.

References

He, P., Zhao, Z., Tan, Y., Hengchao, E., Zuo, M., Wang, J., Yang, J., Cui, S., & Yang, X. (2021). Photocatalytic degradation of deoxynivalenol using cerium doped titanium dioxide under ultraviolet light irradiation. *Toxins*, *13*(7), 1–13. https://doi.org/10.3390/toxins13070481

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