TiO2 Photocatalyst Degradation of β-Carboline

By Noah Ballesteros and Dr. Juan Navea

Saratoga Springs High School

1 Blue Streak Blvd. Saratoga Springs, NY 12866

Review of Literature

Pollution is a big problem all over the world today that has various negative effects; from making water undrinkable to making ecosystems unhabitable (Mafra, 2021 and Nuñez, 2010). Pollution has become such a problem that in 2017, UNICEF reported that 785 million people lacked access to basic drinking water services (Mafra, 2021). Just from this, it can be seen just how influential water purification research can be; not just impacting one, isolated location, but communities world-wide who need to be provided with this simple human right.

Pollutants such as per- and polyfluoroalkyl substances (PFAS), which are commonly used in many firefighting foams (used around Saratoga Springs), are known as “forever chemicals, having extremely long half-lives (Nuñez, 2010). However, photocatalysts may have the potential to degrade this pollutant, as they have been shown to degrade other model and actual pollutants such as 2-propanol (isopropyl alcohol) (Kamegawa, 2010), acetaminophen (González-Muñoz, 2022), diclofenac (González-Muñoz, 2022), and estrogen (Mafra, 2021).

Over the course of 50 plus years, knowledge of titanium dioxide (TiO2) photocatalysis has expanded with so many scientists interested in the field. The first article that suggested the existence of TiO2 photocatalysis was back in 1972 that mentioned the “Honda-Fujishima effect” (Ohtani, 2014). This first paper didn’t explicitly mention photocatalysis but promotes it as a growing interest among scientists. It focused on a titania anode under photoirradiation; similar to photocatalysis (Ohtani, 2014).

In many research articles, photocatalysis is essentially described as the acceleration of a photoreaction by the presence of a catalyst (Castellote, 2011); in this case, a TiO2 photocatalyst (previously, a TiO2/N6 cellulose-paper photocatalyst was going to be used but to reduce the variability in surface area of the paper, TiO2 powder will be used instead as its surface area can be measured in a simpler manner). Although TiO2 has been shown to be cancerous, this occurs only in large quantities, known as excessive lung overload and seen as this study only uses 0.016g of TiO2, a carcinogenic effect is very unlikely.

Looking deeper, the process of photocatalysis is fairly simple: the repetition of many oxidation-reduction reactions (redox reactions) that are used to decompose both organic and inorganic compounds (Castellote, 2011) (although, the process occurs more efficiently in organic compounds). In order for this degradation to occur, sufficient energy must be supplied from a photon to promote an electron from the valance band to the conduction band, leaving a hole behind in the valence band (Castellote, 2011).

The degradation of pollutants through photocatalysis can happen within two mediums: liquid and air pollutants. Looking at air pollutant applications, different solutions such as photocatalytic paints and concrete have been utilized (Song, 2020 and Visali, 2020). These photocatalysts work in the same manner as liquid/water photocatalysts; they decompose pollutants through repeated redox reactions and convert harmful compounds like carbon dioxide (CO2) into harmless products (Visali, 2020). Liquid and air photocatalysts are commonly tested in the same way: applying some sort of methyl stain or model pollutant to the photocatalyst in order to test its effectiveness degradation qualities (Al-Namshah, 2021) (Visali, 2020).

Photocatalytic enhancement is also being studied in boosting the performance of photocatalysts. The doping process – where impurity atoms of rare earth metals are added to a semi-conductor to manipulate its properties – has been very successful in degrading model pollutants (methyl green) if not more types (Al-Namshah, 2021). Additionally, the use of supports/substrates in photocatalytic research has been used in the production of the photocatalysts. For instance, filter paper has been shown to benefit the fabrication of a certain TiO2 photocatalysts due to its porosity and sustainability (Mafra, 2021).

Due to supply chain issues, this study utilizes a pollutant like PFAS similar in its properties: β-carboline. Differing from previous studies, this experiment offers a look at the degradation of a pollutant similar in the properties an extremely harmful and common pollutant: PFAS. Now, the question that remains is whether the TiO2 will influence the degradation of this compound, or will the sunlight only degrade the model pollutant, or will β-carboline not even be degraded at all.

Hypothesis/Purpose

With this research, the safety of people and the environment is paramount to the purpose of the study. The problem is simple, yet complicated: how can pollutants be degraded in and energy-efficient, environmentally friendly, and cost-effective manner to ensure the wellness and safety of people impacted by PFAS? The goal of this research is to somehow incorporate all these functions, melding them into an effective pollutant degrader in water that specifically degrades β-carboline. It’s known that photocatalysis works best with organic, water-soluble chemicals, so rationally, β-carboline (being both an organic and water-soluble pollutant) will be able to be degraded by this TiO2 powder photocatalyst. If this experiment is successful, all (or at least most of the β-carboline) would be degraded.

Methodology

This study was conducted at Skidmore College with a solar simulator set up. A solar simulator was incased by a cover to prevent any excess light from entering the experiment. The simulator sits above a jacketed beaker with deionized water running through it to keep a steady temperature (22° C). The solution of β-carboline and the TiO2 powder will be placed in the jacketed beaker on top of an orbital agitator that will stir the mixture. Before the experiment begins, the mixture will sit with nitrogen gas flowing through it to remove oxygen to simplify the reaction. Fig. 1 shows this set up.

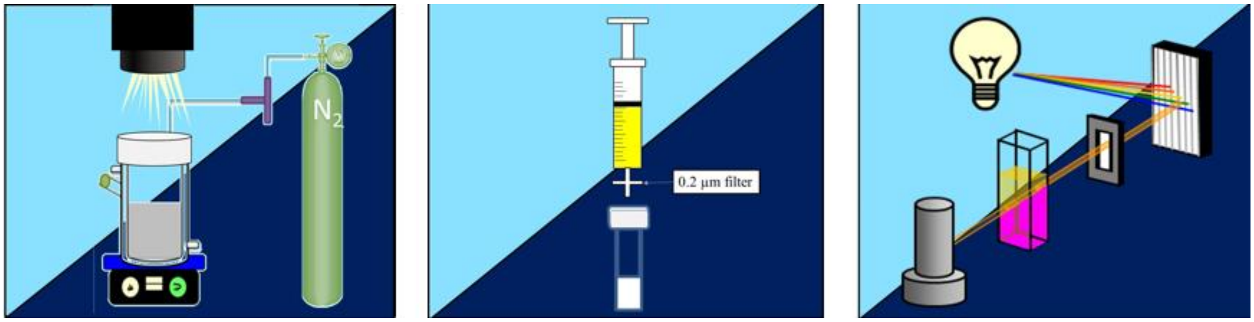

Fig.1 Experiment set up

From the time the experiment begins, samples of the mixture were syringed out and filtered to remove TiO2, leaving just β-carboline alone. The samples were taken at 5, 10, 20, and 40 minutes after the experiment began. After placing the sample in a cuvette, the sample was analyzed using a UV/VIS (ultra-violet/visible light) spectra photometer, which was used to measure the absorbance of light the sample has. This experiment was carried out twice as to verify the result of the experiment. Although a third experiment would have been beneficial, this was not carried out due to time constraints.

In terms of data analysis, Microsoft Excel was used to input and analyze the photocatalytic degradation data. This data was then plotted on line graphs, points located at 5, 10, 20, and 40 min after irradiation. The graphs from the UV/VIS were analyzed at these different sample-extracting times for the differences in the height of their peaks. The baselines of the UV/VIS graphs were normalized around 0% absorbance to create a more easily readable graph.

Results

From the resulting graphs that were plotted, it was concluded that a new, unknown product was formed because of the reaction between β-carboline and TiO2.

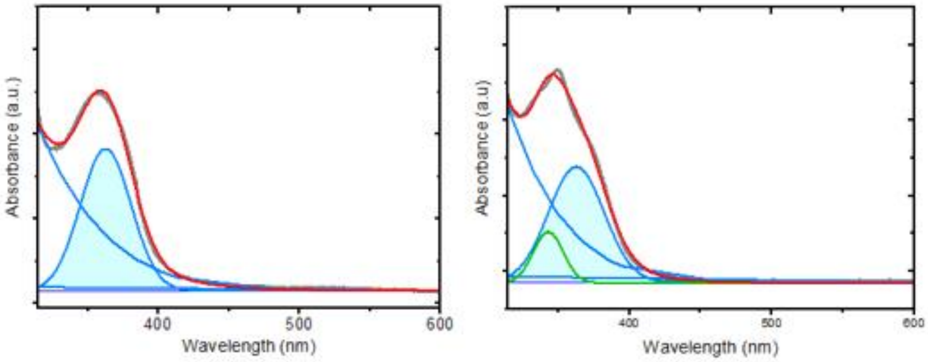

Fig. 2 UV/VIS spectra (blue peak shows β-carboline, black shows TiO2, red shows combined peak, green peak shows unknown substance/left hand peak is at zero min of irradiation and right hand peak at 40 min of irradiation)

As seen in Fig. 1, the small “shoulder” (bulge) on the side of the red peak in both graphs represents the peak of the β-carboline and unknown substances. After the reaction has occurred, a peak indicating the presence of the unknown substance can be clearly seen with an increase in absorbance in Fig. 2.

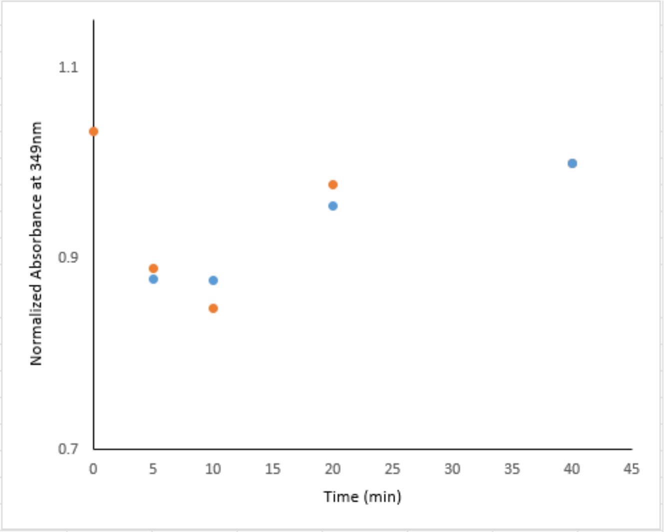

Fig. 3 Absorbance/time points at sample extraction times (experiment 1 in blue and experiment 2 in orange)

Discussion

PFAS is used in many places around the world, specifically in firefighting foams. These foams can easily leak into ground water, which can then find its way into bodies of water, harming the life and ecosystems there. β-carboline was successfully degraded by TiO2 to create a new, unknown substance. If the substance is analyzed and is found to do no harm to the environment, TiO2 could possibly be effective at degrading PFAS.

Future research may focus on extracting water sample in the field, filtering other contaminants for only PFAS can remain. This future will verify the assertion that PFAS can be degraded by TiO2 because it has degraded β-carboline already. Water samples are also more realistic to how photocatalysts can be applied in the field relative to water pollutants and their effects on the environments they pollute.

Conclusion

This experiment consisted of using a solar simulator to irradiate a mixture of TiO2 powder and β-carboline for the degradation of the latter. Simultaneously, the mixture was stirred by an orbital agitator to make sure the solution is in constant motion. Samples of the solution were taken every 5, 10, 20, and 40 minutes for all experiments.

After experimentation was completed, the results were analyzed using Microsoft Excel and it was found that a new, unknown substance was formed for the TiO2/β-carboline reaction. In the future, further analysis of the unknown substance will be carried out along with a follow up study observing the effect of TiO2 on PFAS (whether it can be degraded or not).

Acknowledgements

I'd like to thank my parents, my advisor, Dr. Juan Navea, my Science Research teachers, Ms. Lohnes and Mr. Robinson, and peers. Thanks to my parents (specifically my mom) for driving me to meetings I have with Dr. Navea and for their constant support. Thanks to Dr. Navea for supplying me with even more knowledge on photocatalysis and the lab experience at Skidmore College. Thanks to my Science Research teachers for guiding me on my research journey and giving me much needed constructive criticism. Thanks to my peers for asking questions during my presentations to help me continue to make my research better.

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