

Photocatalytic Degradation of Methylene Blue

Honors Research Thesis

Presented in partial fulfillment of the requirements for graduation *with research distinction* in
Chemistry in the undergraduate college of The Ohio State University

by

Bradley Jones

The Ohio State University

May 2012

Project Advisor: Professor Patrick Woodward, Department of Chemistry

Abstract

Photocatalysis is a booming field of chemistry due to its numerous potential applications. Using light as an energy source to drive a reaction results in chemistry that is much more 'green', helping to eliminate the need for harsh reactants which are often toxic and unrecoverable. Photocatalysis also has applications in the area of renewable energy. A photocatalytic compound could be used to split water into hydrogen and oxygen for energy purposes. This project focuses on the screening of potentially photocatalytic solid state inorganic salts by using these materials to degrade methylene blue, an organic dye, in aqueous solution. Primarily tungstate and vanadate salts were tested for their photocatalytic activity through the degradation of methylene blue in solution under a xenon arc lamp. Select compounds show considerable photocatalytic activity. Solid state synthesized BiVO_4 reduced the absorbance of the methylene blue solution by 30% after 3 hours, the degradation increased to 85% over the same time period when the BiVO_4 catalyst was prepared by an aqueous precipitation route. Vanadate compounds of the form $\text{LiZn}_x\text{Co}_{1-x}\text{VO}_4$ also exhibited photocatalytic activity. Other vanadates and tungstates were evaluated but did not demonstrate photocatalytic activity. These non-active compounds include $\text{Zn}_{1.5}\text{VO}_4$, $\text{Zn}_{1.35}\text{M}_{0.15}\text{VO}_4$ (M=Ni, Cu), and $\text{Na}_{0.5}\text{Ce}_{0.25}\text{A}_{0.25}\text{WO}_4$ (A=La, Ce, Bi), amongst others.

1. Introduction.

1.1 Catalysts and Sustainability

Catalysts are materials which are able to direct chemical reactions by providing new reaction pathways without being consumed themselves. Because of this, catalysis is a technology that will drive the future as society presses forward toward more sustainable energy and production¹. Uses of catalysts range from the chemical industry, to energy, to transportation as catalysts are powerful tools that allow new ways to achieve what was once difficult. Catalysts by definition are sustainable as they are not consumed themselves during a reaction. This is of crucial importance as society progresses. Society needs to be able to use resources efficiently and keep long term sustainability in mind. Catalysts promote both efficiency and sustainability by reducing wastes and providing alternative routes. Catalysis promotes “green chemistry”² which can be defined as using chemistry to circumvent pollution and to utilize environmentally safe processes. Improvements in this “green chemistry” are necessary as are metrics³ for analyzing this ‘greenness’ to ensure that sustainability is moving in the correct direction. As the government presses forward on sustainability and efficiency requirements⁴, the importance of green chemistry and catalysis is growing, as these two fields have the ability to drive innovation to keep producing more products with lower material costs and higher yields.

1.2 Applications of Photocatalysts

Photocatalysts are of particular interest because one of the reactants, light, is in essentially limitless supply. Photocatalysts have widely varying applications. One such application is waste water treatment⁵, which was developed and used in Japan in as early as 2001. This reactor decomposes dioxins and environmental hormones using UV light instead of

incineration or harsh chemicals. Photocatalysts have also been identified as able to degrade toxic chlorinated carbons such as carbon tetrachloride⁶, generating relatively harmless carbon dioxide and hydrochloric acid as byproducts. Using photocatalysis to safely degrade chlorinated hydrocarbons would cut down on a tremendous amount of waste, as these compounds are common chemical solvents. Additionally, photocatalysts can be used for sterilization of microbial cells⁷. This was achieved using a titanium dioxide photocatalyst to oxidize a coenzyme, preventing respiration in the cells. Finally, photocatalyst find tremendous potential in their use to split water into its elements, hydrogen and oxygen⁸. Much effort has been put into this 'artificial photosynthesis' where light is turned into an energy source through artificial means. The products generated, hydrogen and oxygen, have wide uses, including in fuel cells to power cars or generate electricity. Photocatalysts have the potential to remove us from dependence on the dwindling supply of fossil fuels and move toward abundant, cheap energy.

1.3 Mechanisms of photocatalysis and project goals

Photocatalysis is driven by the generation of electrons and holes through the absorption of light⁹. As an electron is excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), or other unoccupied orbital, a hole, the absence of an electron, is created where the electron used to be. These electrons and holes can then react with water or nearby species to create radicals, which trigger further reactions. Because photocatalysis relies on the generation of these electrons and holes, many of the improvements to photocatalysts are done through attempting to manipulate the band gap in order to absorb more of the available light, especially visible light, as visible light is readily available from the sun. The ability of a material to separate the electrons from the holes is also crucial. If recombination occurs too easily, there will be no opportunity for reaction to occur.. This project will focus on

changing band gaps to affect photocatalysis. Compounds with similar crystal structure but different site substitutions will be tested to observe the effect of band gap on photocatalytic activity. Additionally, a variety of photocatalysts will be screened in order to find the most effective catalysts.

2. Experimental

2.1 Preparation of materials

All samples were prepared through a solid state synthetic route unless otherwise noted. Stoichiometric amounts of starting materials were ground in a crucible before being placed into a furnace. Vanadates and Tungstates were heated at 750 °C for 12 hours. Samples were then checked for phase purity via powder x-ray diffraction. Compounds with mixed phases or starting materials present were reheated for a second time, then re-examined via powder x-ray diffraction.

Aqueous synthesis¹⁰ of BiVO₄ was performed by dissolving 15 mmol Bi(NO₃)₃ · 5H₂O and 15 mmol NH₄VO₃ each in 50 mL 2.0 M HNO₃. The solutions were mixed to yield a yellow solution which was then titrated drop wise through the addition of NH₄OH while stirring to obtain an orange precipitate. The pH of the solution was adjusted to 9 and the slurry was drained and filtered. The recovered material was heated at 200 °C for 3 hours.

Synthesis of NiWO₄ was conducted similarly¹¹, using NiCl₂ · 6H₂O and Na₂WO₄ as starting materials. The reactants were dissolved in distilled water at 60 °C, then combined and allowed to stir as precipitate formed. The precipitate was centrifuged to remove Na⁺ and Cl⁻ ions and was placed in a drying oven to dry before being calcined at 900 °C for 2 hours.

Band gap data was collected with an Ocean Optics USB4000 equipped with a DH-2000-BAL UV-VIS-NIR light source operating from 250-800 nm. Reflectance data was then converted to absorbance via the Kubelka-Monk function, $F(R)=(1-R)^2/(2R)$. The absorbance was extrapolated at the steepest slope out to zero absorbance to obtain the band gap.

2.2 Measurements of photocatalytic activity

All photocatalytic measurements were carried out in methylene blue solution contained in a quartz vessel to allow for transmittance of UV light. A 10 mL aliquot¹² from a 100 mg/L methylene blue stock solution was diluted to a volume of 100 mL using distilled water for a methylene blue concentration of 10 mg/L. The quantity of catalyst was kept the same throughout the experiment, using 0.617 mmol catalyst for each degradation. The catalyst and methylene blue solution were allowed to stir in the dark for 30 minutes prior to illumination to allow for adsorption of the methylene blue onto the surface of the catalyst. The vessel was then illuminated by a 150 W xenon arc lamp while stirring. Aliquots of the solution were collected every 30 minutes for a total of 180 minutes. The aliquots were centrifuged to separate any catalyst present placed into a UV-Vis spectrophotometer to check for the absorbance of methylene blue. The UV-VIS data was collected using an Ocean Optics USB4000 equipped with an Ocean Optics ISS-UV/VIS light source with a wavelength range of approximately 300-900 nm. Degradation of the methylene blue dye was tracked by its absorption peak at 665 nm. This absorption data was used in the determination of degradation of the dye through comparison with the absorbance at a certain time as a percentage of the initial absorbance.

3. Results and discussion

3.1 Degradations using BiVO₄

The initial focus of this investigation was BiVO₄, which had shown the strong photocatalytic degradation of methylene blue on a per mole basis in a previous study¹³. Optimizations of the procedure were performed using BiVO₄ as a catalyst to determine the optimal number of moles of to prevent oversaturation. This investigation is summarized in Figure 1.

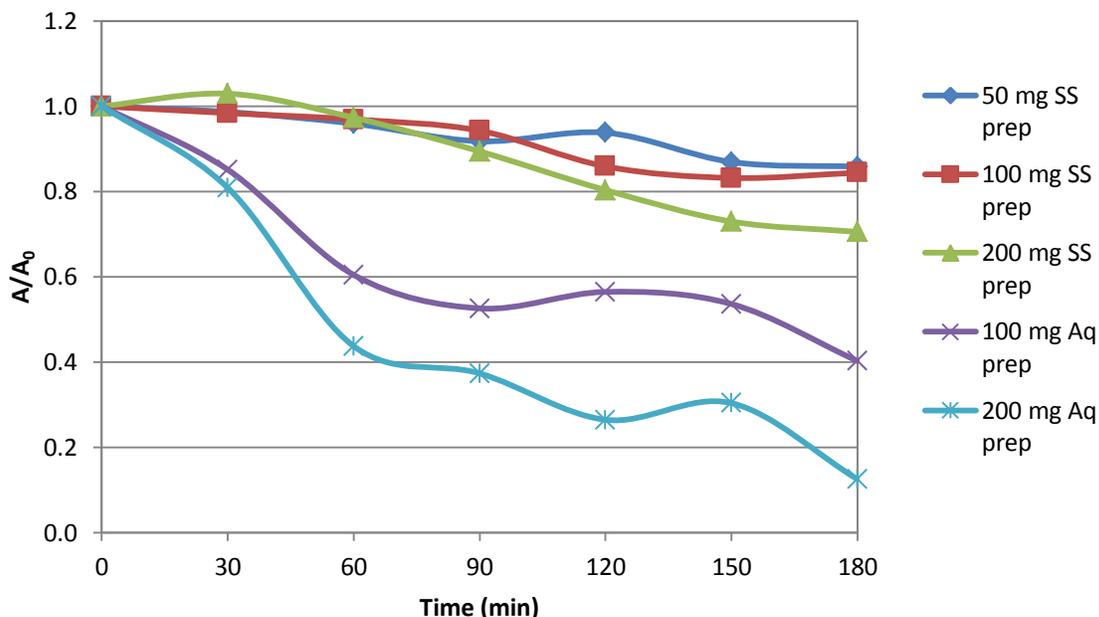


Figure 1. Degradations of methylene blue with varying amount of BiVO₄ catalyst, prepared both through the solid state route and the aqueous route.

This investigation led to the use of 200 mg BiVO₄ as the standard number of moles to be used for the degradation. This quantity was selected for its increased activity to achieve greater degradation in the time frame allotted. Aqueous synthesized BiVO₄ catalyst was tested and performed as a much stronger photocatalysis, degrading the absorbance of the dye more than the

BiVO₄ obtained from the solid state synthesis by a factor of three, 87% degraded vs. 29% respectively. It is believed that this increase in activity is due to an increase in surface area, as increasing surface area has been seen to cause an increase in photocatalytic activity¹⁴.

Further tests were performed with BiVO₄ to test for the reproducibility of the data collected; these trials are summarized in figure 2. Three trials of degradation were performed with the BiVO₄ (aqueous synthesized) catalyst. These trials had good agreement, with 88%, 87%, and 82% of the absorbance of the methylene blue solution degraded after 180 minutes.

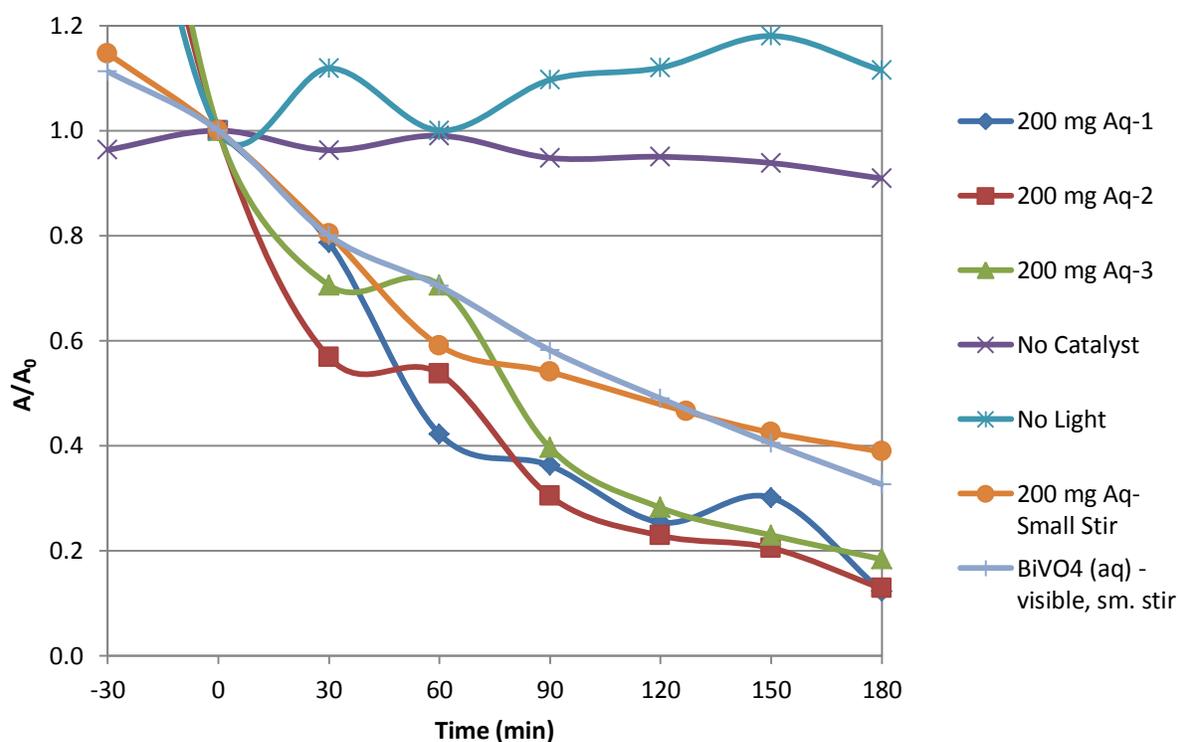


Figure 2. Degradations using BiVO₄ catalyst to test for reproducibility as well as adsorption and photolysis of methylene blue.

Experiments were also carried out to ensure that the activity seen was indeed photocatalytic in nature. Methylene blue solution was illuminated without a catalyst to observe any photolysis effects of degrading without a catalyst. This photolysis effect was small, amounting to a 9% reduction in absorbance over the course of 180 minutes. The vessel was also

charged with catalyst and methylene blue solution but not illuminated in order to test for adsorption effects. The absorbance of methylene blue did not decrease without light, indicating that the decreases observed for other trials are photocatalysis and not continued adsorption of the methylene blue onto the surface of the catalysis.

The effects of using visible light are also shown in figure 2. When a 400 nm cutoff filter was used, the BiVO_4 (aqueous prepared) catalyst degraded the dye slightly more than without the cutoff filter. This shows that the BiVO_4 catalyst is active for photocatalysis, which is desired in a photocatalytic material. These results also show the sensitivity of the system; even a change in the size of the magnetic stir bar can impact the outcome by as much as 60% as observed here. This suggests that the rate of degradation is largely limited by the surface area of the catalyst; degradation increases when stirred more vigorously, which introduces more loose particles into solution, increasing surface area.

3.2 Tungstates

An earlier photocatalytic screening showed promise from a variety of tungstate based photocatalysts. Compounds of the form $\text{M}_{0.5}\text{A}_{0.25}\text{B}_{0.25}\text{WO}_4$ (M= Na, Ag, A= La, Bi, Ce, B= La, Bi, Ce) were investigated to the ability to manipulate their band gaps. Based on the metals selected, the band gaps ranged from 4.52 eV for $\text{Na}_{0.5}\text{La}_{0.5}\text{WO}_4$ to 2.57 eV for $\text{Ag}_{0.5}\text{Ce}_{0.25}\text{Bi}_{0.25}\text{WO}_4$. Substitution of the sodium atoms or the lanthanum atoms by silver or bismuth and cerium respectively lowered the band gap through the introduction of valence electrons found in these atoms. The band gaps for these compounds are listed in table 1 with plots of their solid state UV-Vis reflectance following in figure 3.

$\text{Na}_{0.5}\text{La}_{0.5}\text{WO}_4$	$\text{Ag}_{0.5}\text{Ce}_{0.25}\text{La}_{0.25}\text{WO}_4$	$\text{Na}_{0.5}\text{Ce}_{0.25}\text{Bi}_{0.25}\text{WO}_4$	$\text{Ag}_{0.5}\text{Ce}_{0.5}\text{WO}_4$	$\text{Ag}_{0.5}\text{Ce}_{0.25}\text{Bi}_{0.25}\text{WO}_4$
4.52 eV	2.92 eV	2.76 eV	2.7 eV	2.57 eV

Table 1. Band gaps for select tungstate compounds

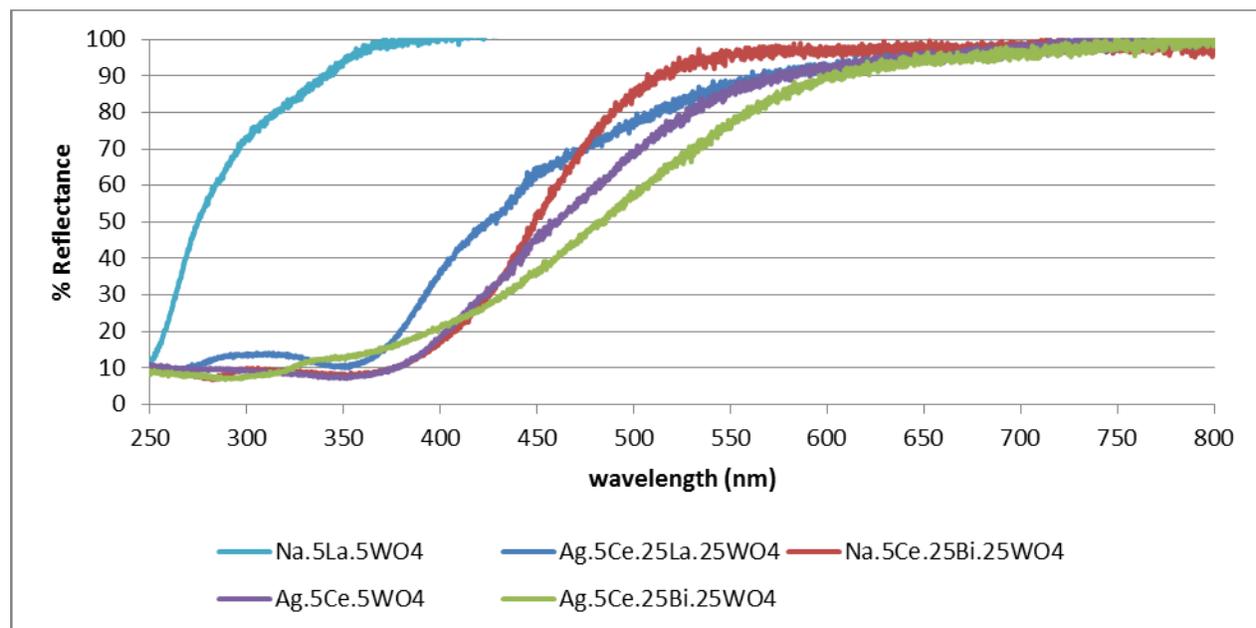


Figure 3. Solid state UV-Vis data for select tungstates.

Introduction of the valance electron containing metals pushes the band gap toward the visible region, 400 nm or 3.10 eV. The effects of these additions are mostly cumulative and show that incorporation of bismuth, even at the cost of cerium, will result in an overall smaller band gap. Substitution with these ions gives rise to materials with smaller band gaps which can absorb more of the available light, be it from the sun or the light source here, increasing their potential value as photocatalysts.

It was observed previously that some of the more substituted tungstates had smaller band gaps, well into the visible region, and these showed some photocatalytic activity under the tungsten lamp. However, when these compounds were tested under the xenon arc lamp as described above, very little photocatalytic activity was observed. Degradation results for the

tungstates can be seen in figure 4. The only tungstate based photocatalyst to show degradation greater than that of the photolysis of methylene blue was $\text{Ag}_{0.5}\text{Ce}_{0.5}\text{WO}_4$, which degraded the absorbance by only 11%, compared to the 9% of photolysis. It is unclear why the tungstates had minimal photocatalytic activity.

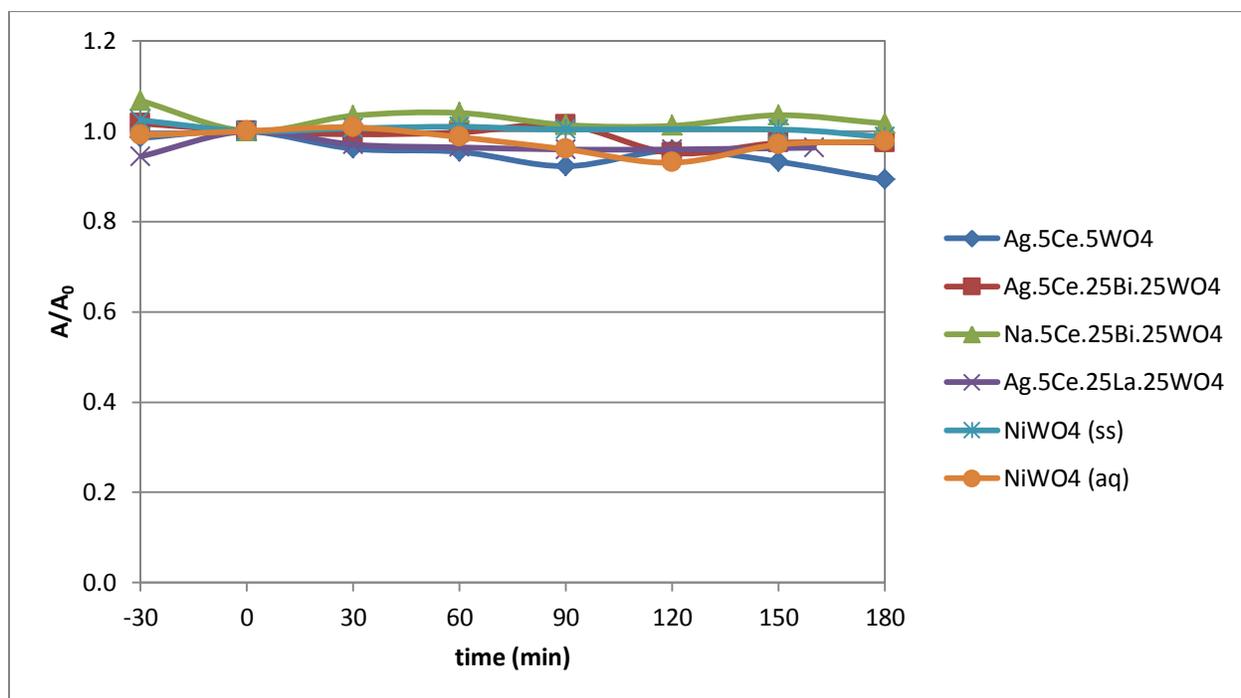


Figure 4. Degradation of methylene blue by select tungstates.

3.3 Vanadates

Following the success of BiVO_4 and the lack of activity in the tungstates, the focus of the screening shifted toward vanadates. A variety of vanadates were tested for photocatalytic activity, generally ZnVO_4 and variants where nickel or copper are substituted for zinc. The band gaps of these vanadates were also examined and are shown in table 2 while the solid state UV-Vis reflectance of the vanadates is shown in figure 5.

Compound	Band gap (eV)	Compound	Band gap (eV)
Zn _{1.5} VO ₄	3.2	LiZnVO ₄	3.39
Zn _{1.35} Cu _{0.15} VO ₄	3.01	LiZn _{0.85} Co _{0.15} VO ₄	2.45, 1.64 ^[1]
Zn _{1.35} Ni _{0.15} VO ₄	2.68	LiCoVO ₄	1.57

Table 2. Band gaps for select vanadate compounds

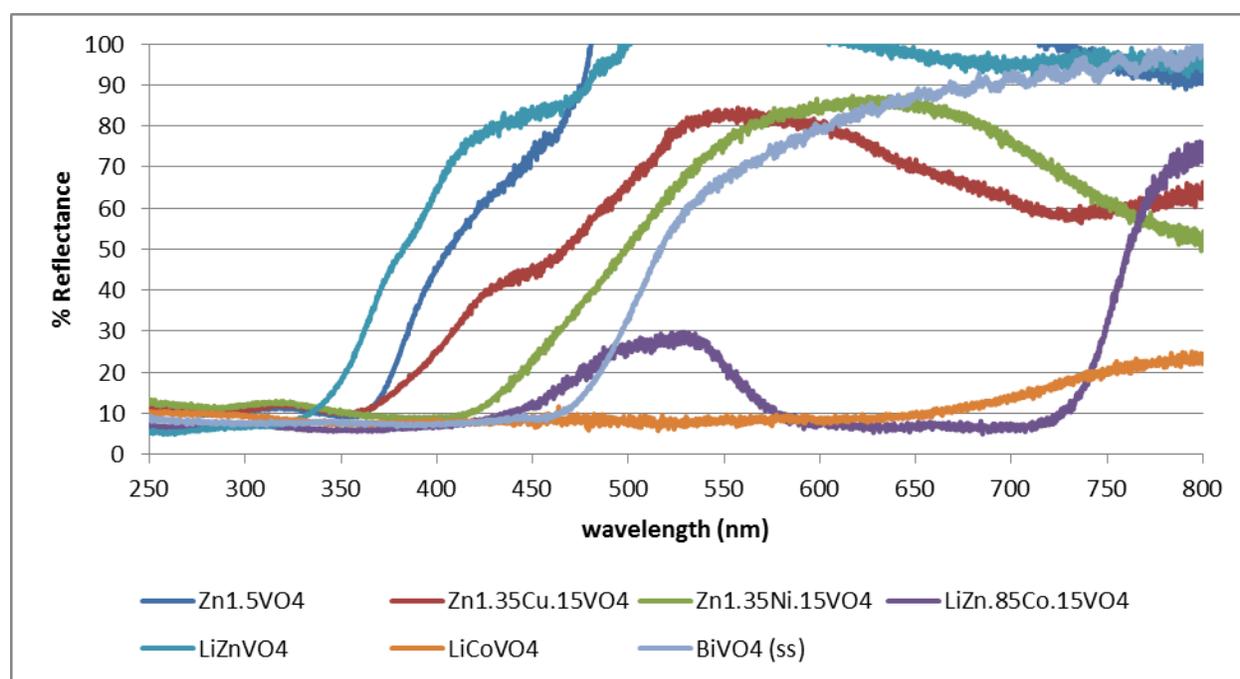


Figure 5. Solid state reflectance data for vanadates tested for photocatalytic activity.

The band gaps for the vanadates are most interesting when compared to the photocatalytic activities for these compounds, shown in figure 6.

^[1] This absorbance is a d-to-d transition

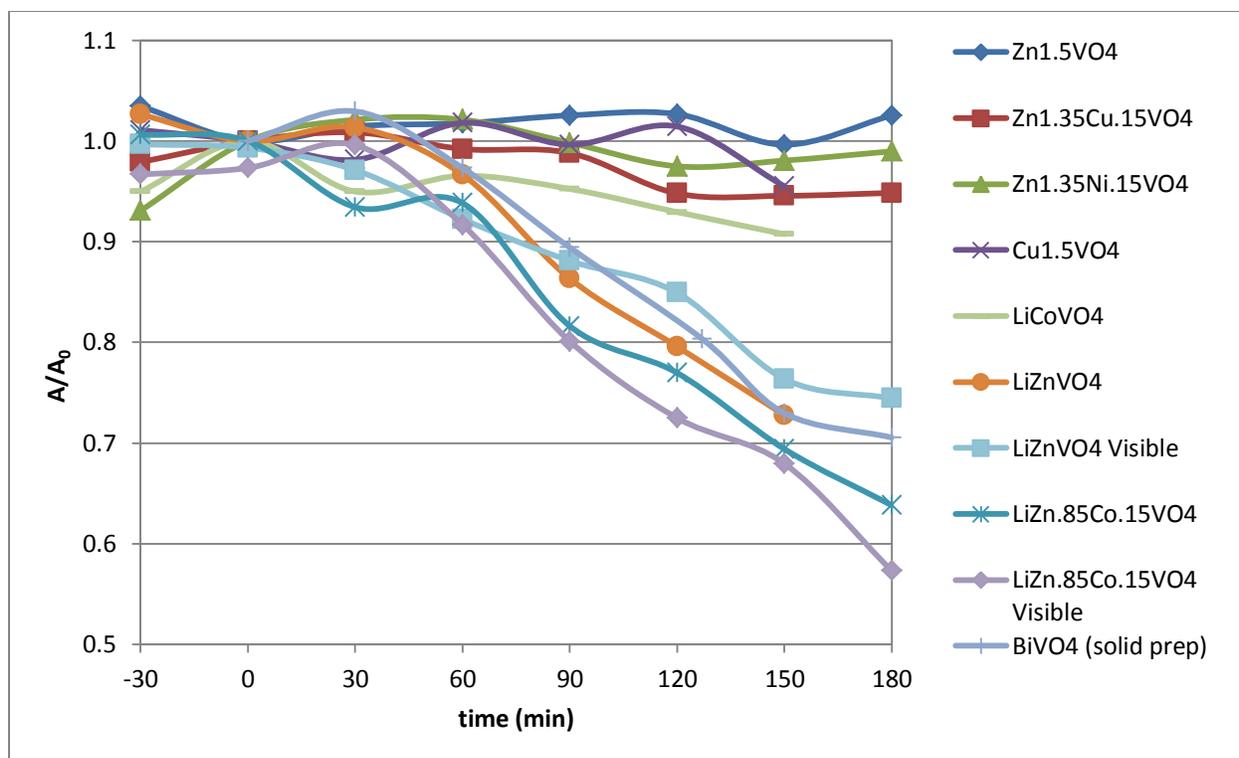


Figure 6. Degradations of methylene blue by select vanadates.

Only BiVO₄ and LiZnVO₄ as well as cobalt doped LiZnVO₄ were photocatalytically active. However, these compounds showed considerable photocatalytic activity. LiZnVO₄ was surprisingly active, even in visible light, despite its large band gap of 3.39 eV. The visible light which the cutoff filter allowed to pass would not have enough energy to cause excitations from the HOMO to the LUMO, so there seems to be another effect at work. LiZnVO₄ and LiZn_{0.85}Co_{0.15}VO₄ both showed activity that met or exceeded that of solid state produced BiVO₄; the same synthesis conditions as the vanadates. The LiZn_{0.85}Co_{0.15}VO₄ sample has a unique spectra where it has two absorptions, one occurring at 2.45 eV and the second at 1.64 eV, and this compound was the most photocatalytically active of all the compounds tested. It is thought that the second, lower energy absorbance is a d-to-d transition. This transition is unlikely to be the cause for the photocatalytic activity, as the LiZnVO₄ sample was also active without having a d-to-d transition, however investigation of this specific activity is outside the scope of the project

Both LiZnVO_4 and $\text{LiZn}_{0.85}\text{Co}_{0.15}\text{VO}_4$ showed considerable photocatalytic activity under visible light. The cobalt doped sample showed improvements under visible light as degradation increased from 36% to 41% of the absorbance while LiZnVO_4 showed a slight decrease, from 27% to 25%, remaining active despite the light not having enough energy to cause HOMO to LUMO excitations. LiCoVO_4 however did not exhibit photocatalytic activity. . The activity of LiZnVO_4 is peculiar because it remains active under visible light, where the incident light does not have enough energy to cause excitations in the band gap. Because of this, it is suspected that the activity of LiZnVO_4 and possibly $\text{LiZn}_{0.85}\text{Co}_{0.15}\text{VO}_4$ is not photocatalytic, but are instead acting as traditional catalysts. In this case, light would be absorbed by methylene blue while LiZnVO_4 acts as a conventional catalyst, instead of absorbing the light itself as a photocatalyst would.

Additional experiments were performed to check for degradation of methylene blue by LiZnVO_4 and $\text{LiZn}_{0.85}\text{Co}_{0.15}\text{VO}_4$ in an environment without light. Plots of absorbance vs. time can be seen in figure 7. Both LiZnVO_4 and $\text{LiZn}_{0.85}\text{Co}_{0.15}\text{VO}_4$ showed some photocatalytic activity, degrading the absorbance of the methylene blue by 20% and 10 % respectively. This suggests that the LiZnVO_4 is behaving like a traditional catalyst instead of a photocatalyst because significant degradation occurred even without illumination.

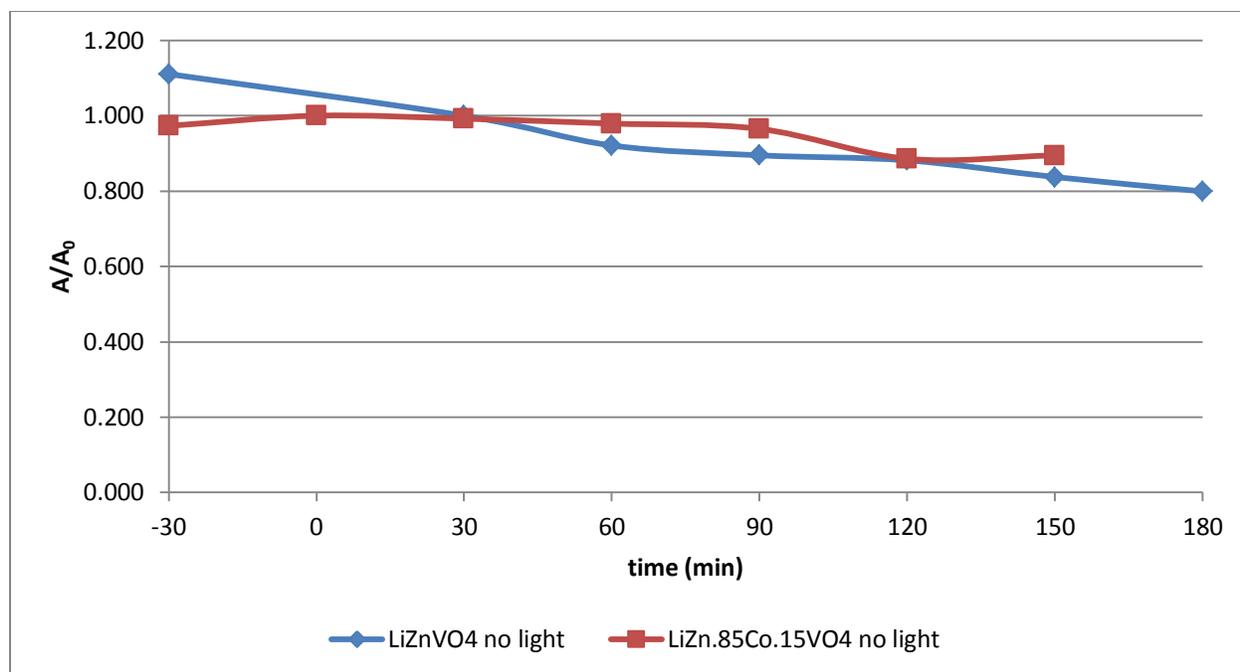


Figure 7. Degradation of methylene blue by select vanadates without illumination.

4. Conclusions and future work

Despite having band gaps that were similar to those of other photocatalysts, none of the tungstates tested showed photocatalytic activity. This may be due to the structure of these compounds; it would be interesting to test tungstates of other crystalline structures to examine whether it is crystal structure that prevents these compounds from exhibiting activity.

Vanadates of the form LiZnVO_4 did show considerable activity and that activity improved upon doping with a transition metal. It may prove fruitful to test other transition metal substitutions to further optimize this catalyst system, as this family of compounds has already been identified as potentially having photocatalytic activity. Improvements could occur from selection of the transition metal for substitution or from different methods of synthesis.

Testing of the materials with different dyes would also be beneficial, especially in the case of LiZnVO_4 . Use of a different dye could help to identify which compounds are behaving as photocatalysts and which compounds are behaving like conventional catalysts. It is suspected that LiZnVO_4 may be a conventional catalyst and a replacement of the dye could help to determine this.

From here, it would be beneficial to perform surface area analyses to determine whether it is surface area at work in the difference between the activities of BiVO_4 produced from different routes. If it is surface area, different synthetic techniques such as aqueous precipitation could be used in order to increase the activity of known catalysts. Surface area measurements would also help identify the compounds with the most potential, should their surface areas be able to be improved.

Finally, these catalysts could be tested for active water degradation through the use of sacrificial reagents such as methanol and AgNO_3 to begin to work toward the ultimate goal: a visible light active, water splitting photocatalyst.

References

- ¹ Centi, Gabriele; Perathoner, Siglinda. Catalysis: Role and Challenges for a Sustainable Energy. *Topics in Catalysis*, 2009, **8**, 948-961.
- ² Perathoner, Siglinda; Centi, Gabriele. Catalysis and sustainable (green) chemistry. *Catalysis Today*, 2003, **77**, 287-297.
- ³ Lapkin, Alexi; Joyce, Lucy; Crittenden, Barry. Framework for Evaluating the “Greenness” of Chemical Processes: Case Studies for a Novel VOC Recovery Technology”. *Environ. Sci. Technol.*, 2004, **38**, 5815-5823.
- ⁴ Green, Jeff. “Better Gas Milage, Thanks to the Pentagon.” *Businessweek* May 17, 2012. May 18, 2012. < <http://www.businessweek.com/articles/2012-05-17/better-gas-mileage-thanks-to-the-pentagon>>
- ⁵ Supsakulchai, A.; Ma, G. H.; Nagai, M.; Omi, S. Performance of titanium dioxide microcapsules as a photo-oxidation catalyst for decolourization of methylene blue. *J. Microencapsulation*, 2003, **20**, 19-33.
- ⁶ Hsiao, C.; Lee, C.; Ollis, D. Heterogeneous Photocatalysis: Degradation of Dilute Solutions of Dichloromethane (CH₂Cl₂), Chloroform (CHCl₃), and Carbon Tetrachloride (CCl₄) with Illuminated TiO₂ Photocatalyst. *Journal of Photocatalysis*, 1983, **82**, 418-423.
- ⁷ Matsunaga, Tadashi; Tomoda, Ryoza; et al. Photoelectrochemical sterilization of microbial cells by semiconductor powders. *FEMS Microbiology Letters*, 1985, **29**, 211-214.
- ⁸ Kudo, Akihiko; Miseki, Yugo. Heterogeneous photocatalyst material for water splitting. *Chem. Soc. Rev.*, 2009, **38**, 253-278.
- ⁹ Yang, M.; Yang, T.; Wong, M. Nitrogen-doped titanium oxide films as visible light photocatalyst by vapor deposition. *Thin Solid Films*, 2004, **469**, 1-5.
- ¹⁰ Zhou, Bin; Zhao, Xu; et al. Visible-light sensitive cobalt-doped BiVO₄ (Co-BiVO₄) photocatalytic composites for the degradation of methylene blue dye in dilute aqueous solutions. *Applied Catalysis B: Environmental*, 2010, **99**, 214-221.
-

¹¹ Yu, Jianqiang; Zhang, Yan; Akihiko Kudo. Synthesis and photocatalytic performances of BiVO₄ by ammonia co-precipitation process. *Journal of Solid State Chemistry*, 2009, **182**, 223-228.

¹² He, H. Y. Luminescence properties of NiWO₄ powders and films prepared with novel methods. *Materials Research Innovations*, 2008, **12**, 138-141.

¹³ Iwase, A.; Kato, H.; Kudo, A. A simple Preparation Method of Visible-Light-Driven BiVO₄ photocatalysts From Oxide Starting Materials (Bi₂O₃ and V₂O₅) and Their Photocatalytic Activities. *Journal of Solar Energy Engineering*, 2010, **132**, 021106-1-5.

¹⁴ Nawi, M. A.; Zain, Salmiah. Enhancing the surface properties of the immobilized Degussa P-25 TiO₂ for the efficient photocatalytic removal of methylene blue from aqueous solution. *Applied Surface Science*, 2012, **258**, 6148-6157.