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Photocatalytic Decomposition of Phenol under Visible and UV Light Utilizing Titanium Dioxide Based Catalysts

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Honors Thesis

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Abstract

Pollution in wastewater effluvia from phenol and phenolic compounds is a common occurrence in many industrial manufacturing plants. Phenol is toxic to human beings as well as a contaminant to the environment, meanwhile, it is difficult to remove from wastewater due to its non-biodegradable nature. To boost the rate of decomposition, various catalytic approaches have been developed. With the interest of decreasing operation cost, titanium dioxide (TiO_2) based catalysts have emerged as good candidates for the photocatalytic process.

In this honors project, a series of TiO_2 based catalysts, including TiO_2 , N- TiO_2 , Cu- TiO_2 , and Cu-N- TiO_2 , were utilized to study the decomposition of phenol. Each catalyst was studied under the visible light (589nm) and UV light (385nm) conditions. The UV-Vis spectrophotometer was used to evaluate the catalytic performance. The results revealed that the addition of nitrogen improved the phenol degradation compared with that of TiO_2 itself. Copper did not show improved photocatalytic performance and requires further investigation.

1.0 Introduction

1.1 Phenol in industry

Phenol (C_6H_5OH) is a carboxylic acid consisting of a phenyl group bonded to a hydroxyl group, shown in Figure 1, which is used to manufacture a wide variety of products. Many industrial processes rely on the use of phenol, such as the petrochemical industry, petroleum refineries, coal gasification operations, liquefaction processes, dye synthesis units, pulp and paper mills and pharmaceutical industries. In addition, phenolic resins are critical in the plywood, construction, automotive, and appliance industries [1]. Its usages can be found in adhesives and sealant chemicals, flame retardants, ion exchange agents, and odor agents. Consumer uses of phenol include wood products, cleaning and furnishing care products, floor coverings, and paints and coatings [2]. Due to the wide range and abundant use of phenol, it is critical to be aware of the dangers of the chemical and effective techniques for disposal.

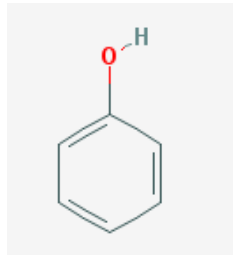


Figure 1. Chemical Structure of Phenol [2]

1.2 Toxicity of phenol

Phenol is a contaminant to the environment and difficult to remove from wastewater due to its non-biodegradable nature. Pollution in wastewater effluvia from phenol and phenolic compounds is a common occurrence in many industrial manufacturing plants. Phenol is a highly corrosive nerve poisoning agent and is known to have harmful short-term and long-term effects on human beings. It is also toxic to aquatic wildlife. The toxic levels range between 10-24mg/L for humans and 9-25mg/L for fish. The lethal blood concentration for humans is approximately 150 mg/100ml [1]. As a result of the toxic and harmful nature

of phenol, it is imperative that phenol is properly removed/decomposed from wastewater before wastewater streams are returned to environment.

1.3 Methods of phenol decomposition

Various methods of phenol decomposition have been studied to remove/reduce phenol concentrations in wastewater streams. Polymerization is a method in which phenol polymerizes in the presence of hydrogen peroxide and enzymes. It is highly effective but costly due to the required enzymes. Biological methods have also been used to carry out decomposition of phenol using activated sludge in membrane bioreactors. This has also proven effective but requires high cleaning expenses due to fouling. Other methods that have been studied include electrocoagulation, extraction, adsorption and ion exchange, and photodecomposition.

Titanium dioxide (TiO_2) is photocatalyst that is commercially available and fairly inexpensive. It is known to initiate the degradation and mineralization of various organic pollutants. As a result, TiO_2 photocatalyzed degradation of phenol in water is a potential method of environmental remediation. However, TiO_2 photocatalyzed reactions with phenol are limited from a low quantum efficiency and need for UV-light [3]. As a result, TiO_2 has been used extensively in combination with other materials. For example, it has been found that activated carbon improves the photocatalytic activity of TiO_2 . Recently, carbon nanotubes (CNT) are also an attractive option due to their electronic, adsorption, thermal and mechanical properties [4]. In addition, photocatalytic applications of various Layered Double Hydroxides (LDHs), including ZnAl, ZnTi, and ZnAlFe, have been reported. Mixed oxides obtained from calcination of transition metal-containing LDHs have also proven to be beneficial to photocatalysis, for example, Zn(Al) [5].

However, the use of UV light to decompose large volumes of wastewater is not a practical. Scientists are continually searching for sustainable technology in chemical/catalytic alternatives that are economically favorable and efficient in the degradation and removal of phenol from water. The goal of this

project was to study the degradation of phenol via photocatalysis utilizing titanium dioxide modified catalysts under UV light as well as visible light. If photodegradation of phenol and other organic compounds can be achieved under visible light, it could be revolutionary to wastewater treatment in industry.

1.4 Objectives

The motivation of this project was primarily to determine the feasibility of using the TiO_2 catalyst for photocatalytic degradation of phenol. The catalysts studied in this project were titanium dioxide (TiO_2), nitrogen modified titanium dioxide (N-TiO_2), copper modified titanium dioxide (Cu-TiO_2), and nitrogen and copper modified titanium dioxide (Cu-N-TiO_2). The influence of nitrogen and copper doping was to be explored and compared under UV and visible light conditions. The effect of irradiation time on degradation was to be considered for catalysts with high activity.

1.5 Rationales

This project focused on finding the catalyst with the highest activity. The following questions needed to be addressed.

- *Does modification with nitrogen and/or copper improve photocatalytic performance?*
- *Can equivalent photocatalytic activity be achieved in the visible spectrum as in the UV spectrum?*
- *Is the catalyst stable over time?*

2.0 Methodology

2.1 Photocatalysis reaction kinetics via titanium dioxide catalyst

In a heterogeneous photocatalytic system, photo-induced molecular transformations or reactions usually take place at the surface of the catalyst. The first step is to excite the system using photons of light. Molecules absorb photons to produce a highly reactive, electronically excited state. The photon requires sufficient energy to promote an electron across the band gap, or the void region between the top of the filled valence band to the bottom of the vacant band. Since TiO_2 has a wide band gap of 3.2eV, visible light is

not sufficient. Therefore, TiO_2 requires light from UV range (wavelength less than 390nm) to initiate the photoreaction. This initial excitation is followed by an electron transfer to the solvent or organic species that is adsorbed on the surface of the catalyst. In the case of TiO_2 , the excited electron reduces an oxygen molecule to O_2^- . Meanwhile the positively charged electron hole (h^+) reacts with water to produce a hydroxyl radical ($\cdot\text{OH}$), as shown in Figure 2. The hydroxyl radical initiates the chemical reactions in the photocatalytic process [6]. The absorption of a photon of radiation occurs very rapidly (on the order of 10^{-15}s), while the subsequent deexcitation occurs much slower. The photochemical reactions occur on the time scale of 10^{-12} to 10^{-9}s [7].

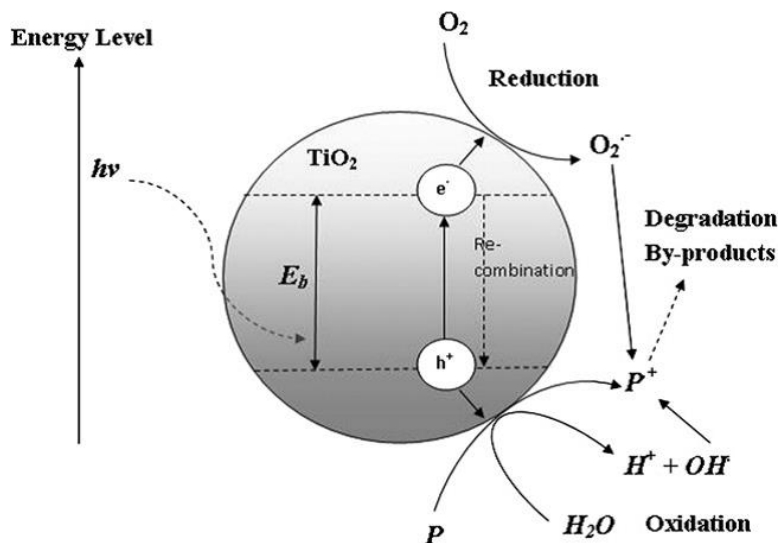


Figure 2. Photocatalytic Process on TiO_2 Catalysts. [6]

The promotion of an electron creates an electron-hole pair which can result in one of two pathways. The desirable pathway is for the photoinduced electron to transfer to the adsorbed organic/inorganic species or to the solvent. In competition with this charge transfer is the undesirable pathway: electron-hole recombination. The efficiency of a photocatalytic process is proportional to the rate of the charge transfer process and inversely proportional to the sum of the charge transfer rate and electron-hole recombination rate. Therefore, recombination of the electron-hole pair needs to be inhibited in order to achieve an efficient

charge transfer process on the catalyst surface. Modifications to semiconductor surfaces with metals or combinations with other semiconductors are proposed to decrease recombination rate [7].

2.2 Phenol decomposition catalyst reaction kinetics

There are two challenges associated with the efficiency of the photocatalytic process. First, the photon of light that strikes the catalyst must have sufficient energy to promote an electron across the band gap. In the case of TiO_2 , visible light is not sufficient and UV light must be used to activate the catalyst. Since UV light on the Earth's surface is less than 5% of the solar spectrum, using UV light for decomposition of wastewater is not practical on an industrial scale [9]. The second challenge is that electron-hole recombination must be slowed down in order to achieve an efficient reaction.

In the case of photocatalytic decomposition of phenol, TiO_2 has been used as the catalyst. The intermediate products formed via the reaction of phenol with $\cdot\text{OH}$ radical ions include hydroquinone (HQ), pyrocatechol (CC), 1,2,4-benzenetriol (HHQ), pyrogallol (PG), 2-hydroxy-1,4-benzoquinone (HBQ), and 1,4-benzoquinone (BQ). These intermediates undergo further photocatalytic oxidation and produce very polar intermediates like carboxylic acids and aldehydes and finally CO_2 and H_2O [8].

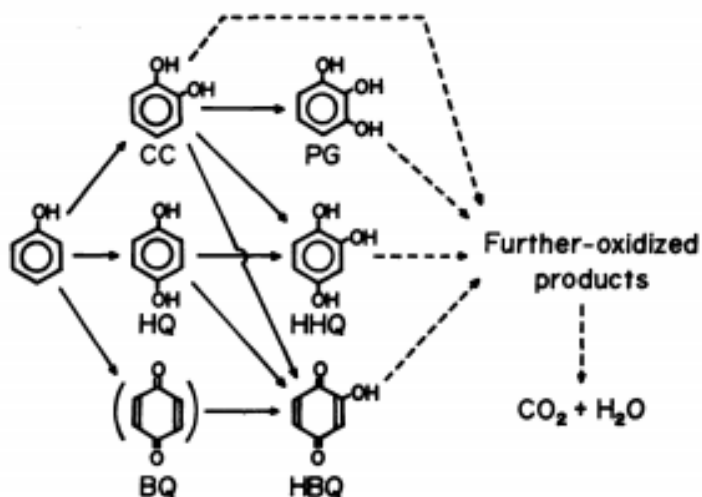
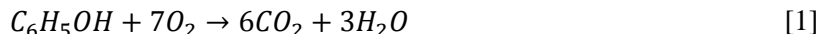


Figure 3. Production Distributions from Phenol Decomposition Reaction [8]

The complete decomposition of phenol can be expressed by Equation 1 [8].



It has been reported that nonmetal doping of TiO₂ catalysts can decrease the band gap energy, thus improving photocatalytic performance under a wider spectrum including the visible light spectrum, which would result in a more efficient utilization of the main part of the solar system [9]. In this project, nitrogen doping of TiO₂ was chosen to see if photocatalytic performance could be improved under visible light conditions.

It has also been found that modifications to semiconductor surfaces by the addition of metals can decrease recombination rate [6]. For example, copper has been reported to effectively reduce the extent of hole-electron recombination by trapping electrons on the surface of the catalyst. In this project, copper doping of TiO₂ catalysts was done to see if photocatalytic performance could be improved in the visible or UV region.

Finally, combining metal and nonmetal methods has been found significantly reduce band gap energy due to the formation of mixed energy levels between the valence band and conduction band of TiO₂. This could further improve photocatalytic response in the visible light region [9]. In this project, TiO₂ catalysts were doped with a combination of copper and nitrogen and studied under both visible and UV light conditions.

3.0 Methods

3.1 Equipment

A 250ml volumetric flask (Pyrex, ±0.12mL) and a mass balance (U.S. Solid Laboratory Equipment, ±0.0005g) was used for this project. To mix the catalyst and solutions well, a magnetic mixer (IKA C-MAG HS10) was used. The UV-1800 Shimadzu Spectrophotometer and UV Probe 2.42 software were used in conjunction to measure absorbance.

3.2 Chemicals

- phenol crystals (Acros Organics, 99.5% extra pure)
- titanium(IV) oxide nanopowder (Aldrich Chemistry, $\geq 99.5\%$, 21nm particle size)
- nitrogen modified titanium dioxide (N-TiO₂) synthesized in the lab via the urea pyrolysis method (reaction temperature of 450°C) with a designed nitrogen loading of 30wt%
- copper modified titanium dioxide (Cu-TiO₂) and copper and nitrogen modified titanium dioxide (Cu-N-TiO₂) synthesized via solid state reaction by mixing and grinding copper acetate, sodium hydroxide, and TiO₂ together in mortar for 30 minutes for a designed loading of 10wt% copper for Cu-TiO₂; and 10wt% copper, 30wt% nitrogen for Cu-N-TiO₂

3.3 Experimental procedure

The concentration of phenol solution was 0.531mM. For each trial, approximately 2.5mg catalyst was mixed with 40mL of phenol solution. The catalyst in solution was mixed using the magnetic mixer for 1 hour without irradiated light, allowing phenol to absorb to catalyst surface. A sample was then extracted via pipette to a cuvette and tested by the UV spectrophotometer. The absorbance across a range of wavelengths between 300 and 240nm was recorded. After 1 hour of mixing without light, either LED visible (589nm) or UV (385nm) light ($I=500\text{ mA}$) was turned on for a determined length of time. The sample was then tested using the spectrophotometer to obtain the peak absorbance. The data obtained was exported to excel and analyzed to calculate final phenol concentration. The final concentration was calculated using Beer's Law shown by Equation 2.

$$A = \epsilon lc \quad [2]$$

Where A is absorbance, ϵ is molar absorptivity ($\text{L mol}^{-1} \text{ cm}^{-1}$), l is path length of sample (path length of the cuvette in which the sample is contained), and c is concentration (mol L^{-1}). It was known the product ϵl was constant since molar absorptivity and path length were constant. Therefore, initial concentration

(0.531mM) was used to solve for constant, ϵl , using initial peak absorbance. Subsequently the final peak absorbance was used to calculate the final concentration after irradiation. The phenol conversion was calculated using Equation 3.

$$\% \text{ conversion} = \frac{C_{\text{Phenol,initial}} - C_{\text{Phenol,final}}}{C_{\text{Phenol,initial}}} \quad [3]$$

Typically, the absorbance was measured for each catalyst over 2 hours under both UV light and visible light. Further, conversion of phenol over time was studied using the catalysts that showed the greatest activity. This was done by irradiating the solution with visible or UV light for 4 hours while measuring concentration each hour.

4.0 Results

4.1 UV-Vis spectrum of pure phenol

A typical UV-Vis absorbance curve for phenol across the wavelength range of 240-300nm is shown in Figure 4. The peak absorbance of phenol is 269nm [5]. As a result, subsequent calculations use the absorbance measured at 269nm to determine phenol concentration at any point along the reaction.

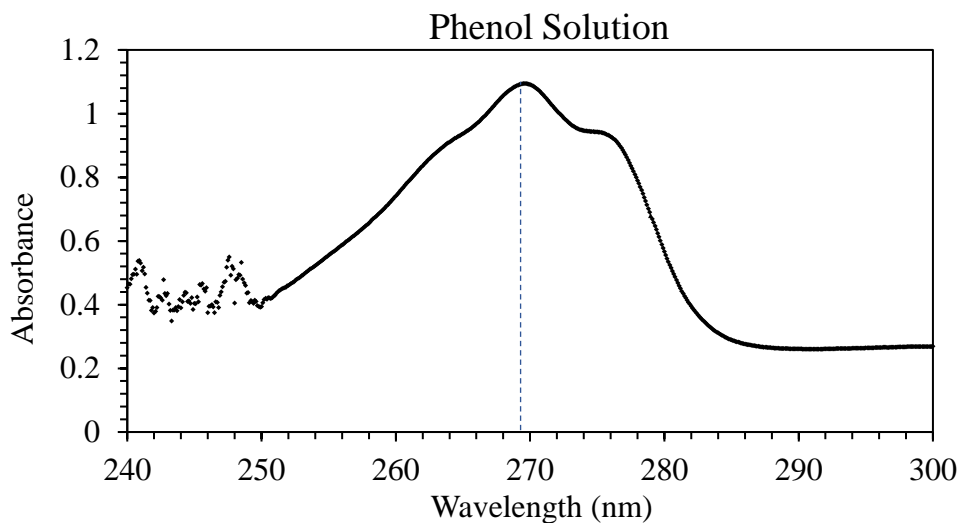


Figure 4. Typical UV-Vis Spectra of Phenol.

4.2 Visible Light (589nm)

4.2.1 Effect of TiO₂ modification

Titanium dioxide was modified with nitrogen and copper alone as well as combined in this project. The modification of the titanium dioxide catalyst with nitrogen was found to improve photocatalytic activity in the visible light region. The amount of phenol decomposed (% conversion) after a 2-hour irradiation period appeared to increase with the presence of nitrogen. The nitrogen modified catalyst (N-TiO₂) resulted in a conversion of 5.7%, which is more than two times greater compared with that of non-modified TiO₂ catalyst (2.2%). The copper-nitrogen modified catalyst (Cu-N-TiO₂) also appeared to improve photocatalytic activity, resulting in a conversion of 5.0%. Error bars on TiO₂ data represent standard deviation of duplicate trials.

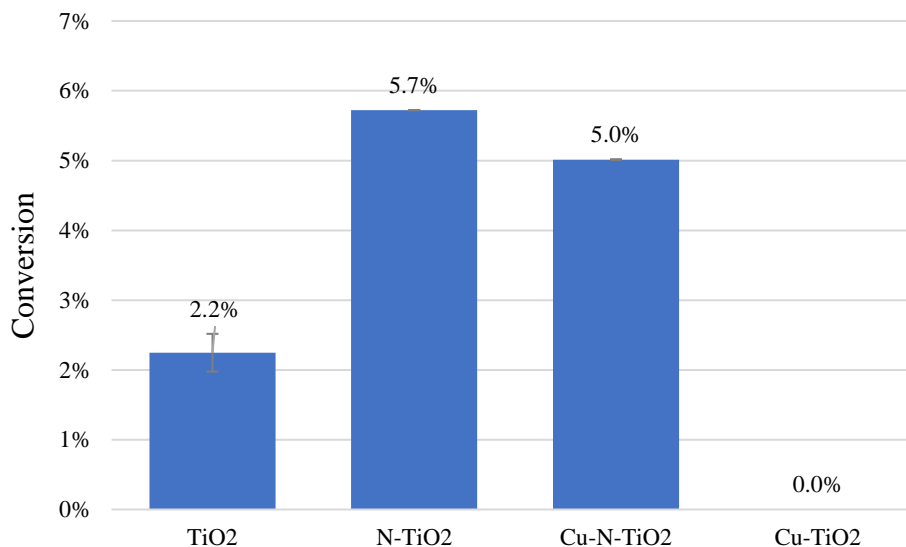


Figure 5. Phenol Conversion using TiO₂ and Modified TiO₂ Catalysts in the Visible Spectrum.

The nitrogen modified catalyst appeared to allow for the greatest phenol conversion as a result of visible light irradiation. The peak absorbance decreased, which indicates phenol degradation occurred, as shown in Figure 6. The absorbance curves for Cu-N-TiO₂ and TiO₂ can be found in the appendix.

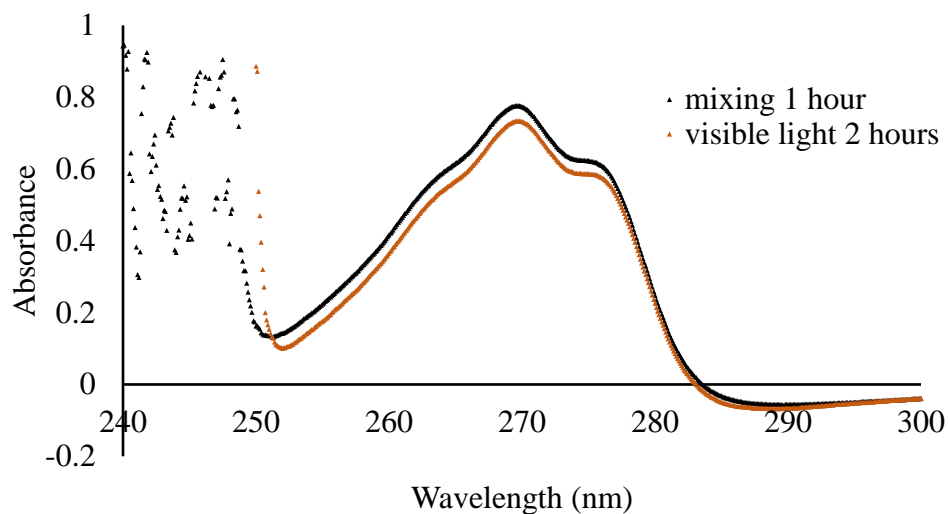


Figure 6. UV-Vis Spectra using $N\text{-TiO}_2$ Catalyst in the Visible Spectrum.

The copper modified catalyst (Cu-TiO_2), on the other hand, appeared to have alternate effects on the absorbance curve. After 2 hours of irradiation under visible light, there was no evident decrease in peak absorbance, however there was a change in absorbance in the 280-300nm range. Since the curve does not appear to be effected from 250-275nm including the peak absorbance, it suggests that visible light had negligible effects on phenol decomposition, as shown in Figure 7. It should be noted that the Cu-TiO_2 catalyst requires further study under these conditions to determine specific effects of copper modification on the solution in the UV spectrum.

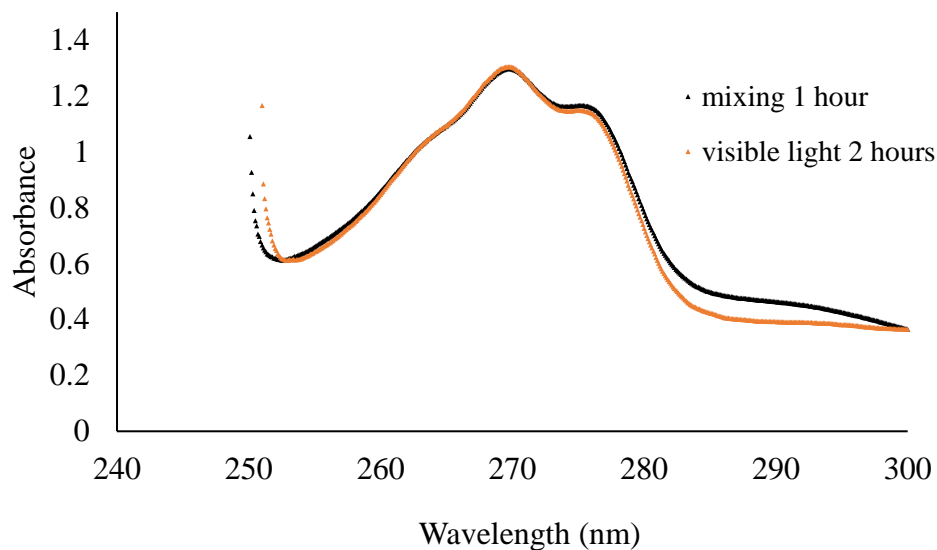


Figure 7. UV-Vis Spectra using Cu-TiO₂ Catalyst in the Visible Spectrum.

4.2.2 Catalytic performance of Cu-N-TiO₂ and N-TiO₂ catalysts

To further study the effects of the nitrogen modified catalysts, the Cu-N-TiO₂ and N-TiO₂ catalysts were irradiated for 4 hours, measuring phenol concentration every hour, as shown in Figure 8. Contrary to the previous results which suggested N-TiO₂ was the most effective catalyst, data suggested phenol degradation occurred at a greater rate using the Cu-N-TiO₂ catalyst. Phenol concentration decreased steadily over the 4-hour irradiation period for both catalysts. The overall conversion for the Cu-N-TiO₂ catalyst and the N-TiO₂ catalyst over four hours was 9.3% and 3.6% respectively.

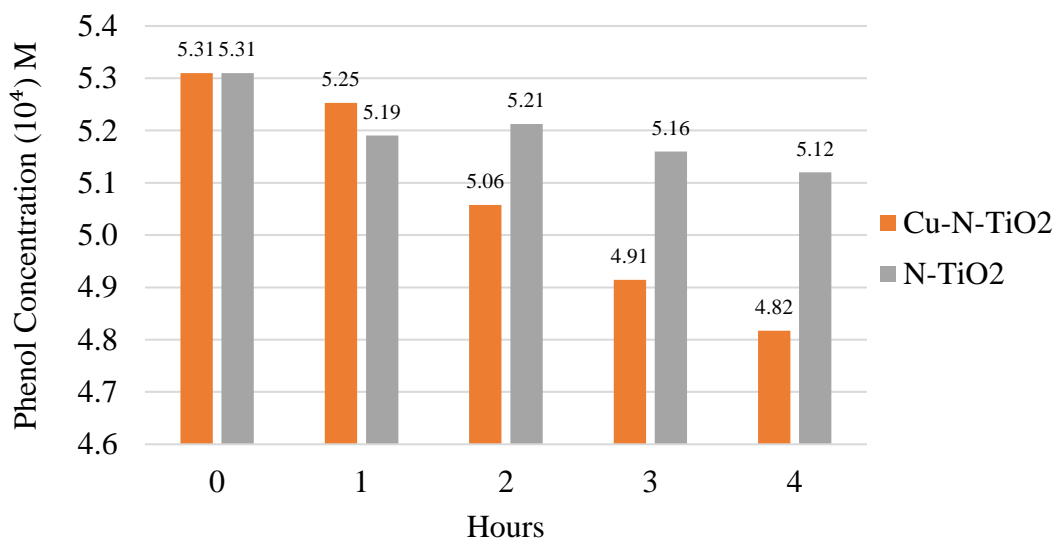


Figure 8. Phenol Conversion over Time using N-TiO₂ and Cu-N-TiO₂ in Visible Spectrum.

4.3 UV light (385nm)

4.3.1 Effect of TiO₂ modification

Similar to its catalytic performance in the visible range, the nitrogen modified catalyst (N-TiO₂) appeared to improve photocatalytic phenol decomposition under UV light conditions. The conversion for the nitrogen modified catalyst (N-TiO₂) was observed to be 5.7%, greatly exceeding that of the non-modified TiO₂ catalyst (0.8%). Interestingly, the copper-nitrogen modified catalyst (Cu-N-TiO₂) didn't appear to promote photocatalysis in the UV spectrum, as shown in Figure 9. Error bars on the TiO₂ catalyst data represent standard deviation of duplicate trials. Absorbance curves obtained from the UV-Vis spectrophotometer can be found in the appendix.

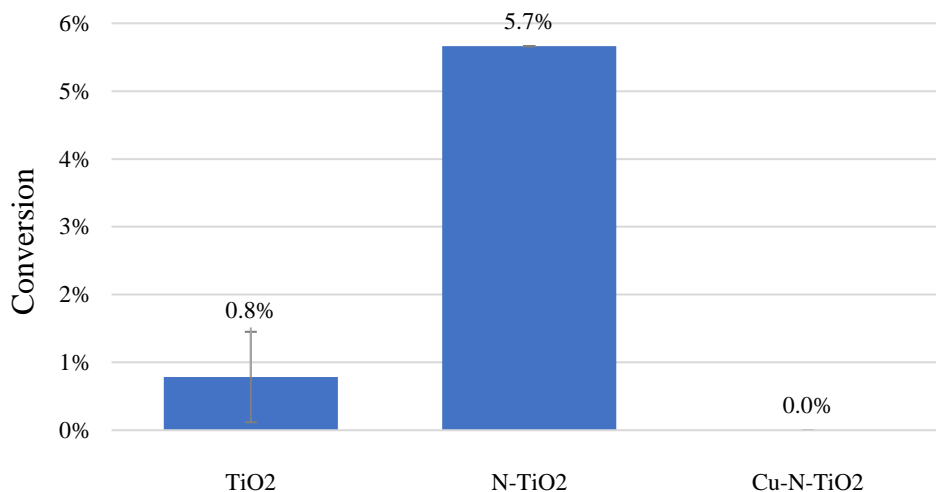


Figure 9. Phenol Conversion using TiO₂ and Nitrogen Modified TiO₂ in the UV Spectrum.

As seen under visible light conditions, the copper modified catalyst showed alternate effects to nitrogen modification. After 2 hours of irradiation under UV light, the peak absorbance did not appear to change, however, absorbance varied in the 275-300nm region, shown in Figure 10. It suggests that the copper modified catalyst had some effects on the solution over time, but requires further investigation to find specific effects of copper in the UV spectrum.

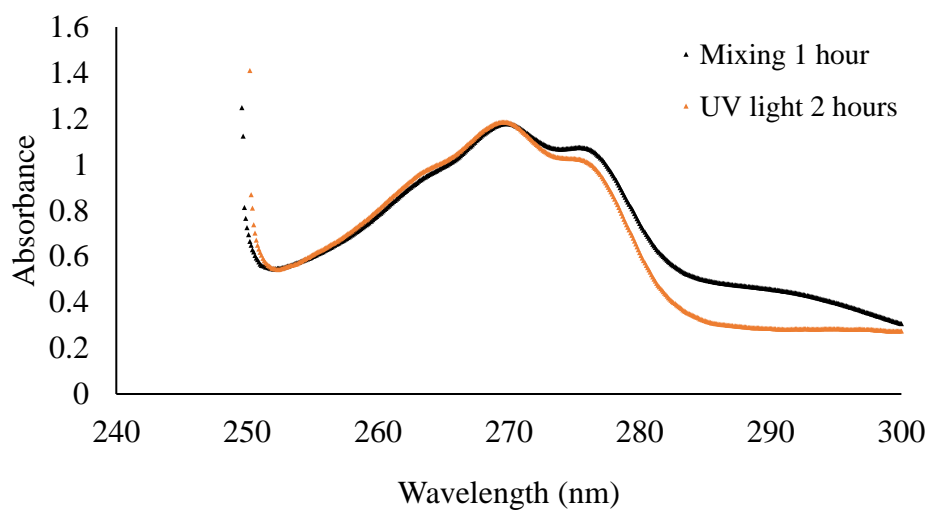


Figure 10. UV-Vis Spectra using Cu-TiO₂ Catalyst in the UV Spectrum.

4.3.2 Catalytic performance of Cu-N-TiO₂ and N-TiO₂ catalysts

To further study the effects of the nitrogen modified catalysts, the Cu-N-TiO₂ and N-TiO₂ catalysts were irradiated for 4 hours, measuring phenol concentration every hour, as shown in Figure 11. Again, data suggests negligible phenol degradation using the Cu-N-TiO₂ catalyst. There is reason to believe error effected these results as concentration appears to increase over time. The N-TiO₂ catalyst appeared to decrease slowly over the irradiation period.

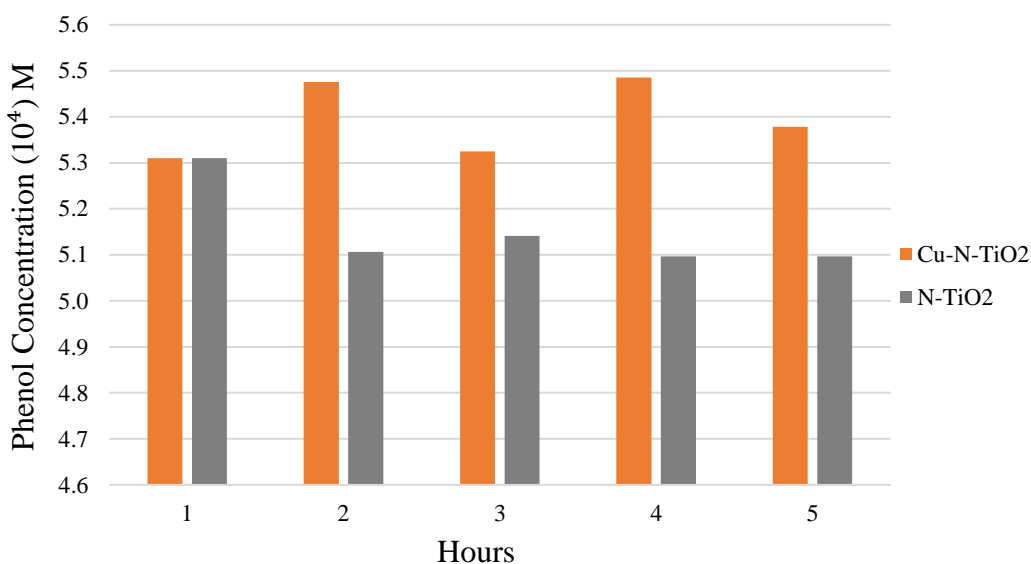


Figure 11. Phenol Conversion over Time using N-TiO₂ and Cu-N-TiO₂ Catalysts in UV Spectrum.

5.0 Discussion

The goal of this project was primarily to determine whether photocatalytic degradation of phenol could be achieved using TiO₂ based catalysts. The study was investigated under UV-light and visible light conditions.

The nitrogen modified catalyst (N-TiO₂) appeared to achieve the best photocatalytic activity in both the visible and UV spectrum after a 2-hour irradiation period. In the visible region, a 5.7% conversion was observed, a magnitude over two times greater than the 2.2% conversion observed for the non-modified TiO₂

catalyst (Figure 5). Similarly, a 5.7% conversion was observed in the UV region, a magnitude over 7 times greater than the 0.8% conversion observed for the non-modified TiO₂ catalyst (Figure 9). This suggests that nitrogen may have effectively decreased the band gap energy of the catalyst, allowing electrons to be promoted under visible light wavelengths (589nm) and subsequent degradation to occur. Over a 4-hour irradiation period in the visible light region, it was found that phenol concentration decreased steadily over time, as shown in Figure 8. The overall conversion after 4 hours was 3.6%, lower than the conversion observed from the 2-hour irradiation period. In the UV region, phenol concentration also decreased over a 4-hour irradiation period and an overall conversion of 4.0% was observed (Figure 11). Again, a conversion less than that observed over the 2-hour irradiation period. The reason the observed overall conversion is less than expected is likely due to sources of error that may have affected this project and will be discussed subsequently.

Errors are likely associated with limitations of the equipment. Since the project was done with very dilute phenol concentrations on the order of 10⁻⁴ M, it is possible that variation was observed due to limitations of the spectrophotometer used. An additional source of error may result from absorption effects. Phenol likely absorbed onto the surface of the catalyst while solution underwent one hour of mixing with no light irradiation. Therefore, the first reading recorded using the UV-Vis was taken while phenol was likely adsorbed to the catalyst surface. Once light was irradiated, it is possible that the increasing of temperature in solution caused phenol to desorb from the catalyst. The second reading taken by the UV-Vis may have been affected by the adsorption-desorption process.

The copper and nitrogen modified catalyst (Cu-N-TiO₂) also appeared to improve photocatalytic activity in the visible light region. After a 2-hour irradiation period of visible light, a 5.0% conversion was observed, approximately double that of the non-modified TiO₂ catalyst (Figure 5). Further, after a 4-hour irradiation period, a steady decrease in phenol concentration was observed and overall conversion was 9.3% (Figure 8). This indicates that nitrogen may have decreased the band gap energy, therefore allowing the degradation reaction to occur under visible light conditions. However, the Cu-N-TiO₂ catalyst did not

appear to promote photocatalysis in the UV region. Negligible conversion was observed over the 2-hour irradiation period (Figure 9), as well as over the 4-hour irradiation period (Figure 11). In fact, concentration appeared to increase marginally over time, which is strange. This is further evidence that error played a role in this project as discussed previously. The discovery of negligible conversion in the UV region suggests the ratio of copper to nitrogen modification on the catalyst was not optimal. Continuation of this project would require a systematic study on the optimal ratio of copper to nitrogen that would most effectively improve photocatalytic activity.

The copper modified catalyst (Cu-TiO₂) demonstrated unexpected catalytic performance results. Based on the UV-Vis data, the absorbance under wavelengths of 280-300 nm was higher before irradiation compared with that after irradiation, especially in the case of UV irradiation (Figure 10). Meanwhile, the peak absorbance appeared to remain approximately the same. Further research is required to explain these effects.

6.0 Conclusions

This study explored the feasibility of using visible light to degrade phenol in wastewater via photocatalysis. While TiO₂ is a commercial catalyst, commonly used and widely studied in photocatalysis, it is not effective under visible light conditions. As a result, the effect of copper and nitrogen modification to the TiO₂ catalyst was studied under visible and UV light conditions. The catalysts studied were: TiO₂, N-TiO₂, Cu-TiO₂, and Cu-N-TiO₂. It was found that nitrogen is an effective modifier. Data suggested nitrogen may decrease the band gap energy, allowing the photocatalytic process to occur in the visible region. Copper was not found to have substantial effects on degradation and requires further study. The Cu-N-TiO₂ catalyst needs to be further studied to optimize the copper to nitrogen ratio and improve photocatalytic performance. The ability to achieve efficient photocatalysis in the visible region could be revolutionary to wastewater treatment in industry as visible light is free and readily available.

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Appendix

Visible Light Conditions

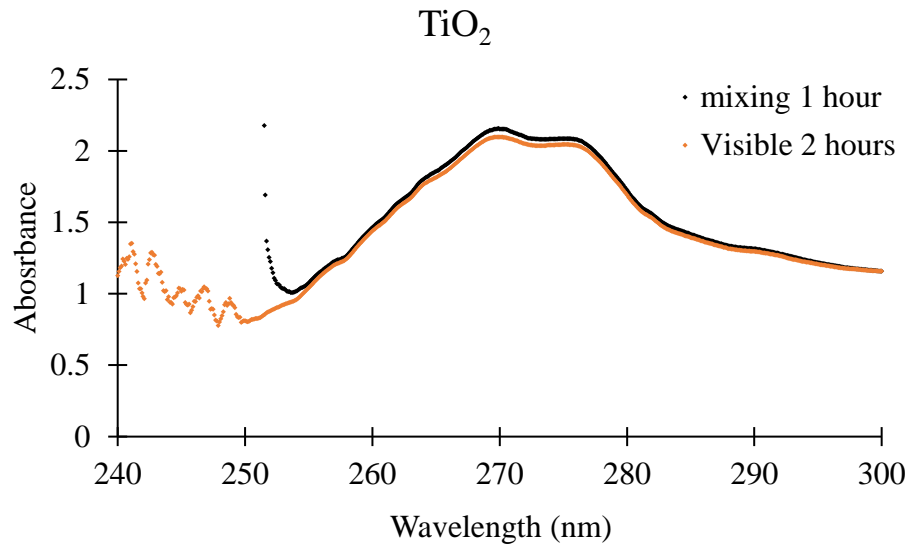


Figure 12. The UV-Vis Absorbance Spectra using the TiO_2 Catalyst in the Visible Spectrum (2-hour irradiation period).

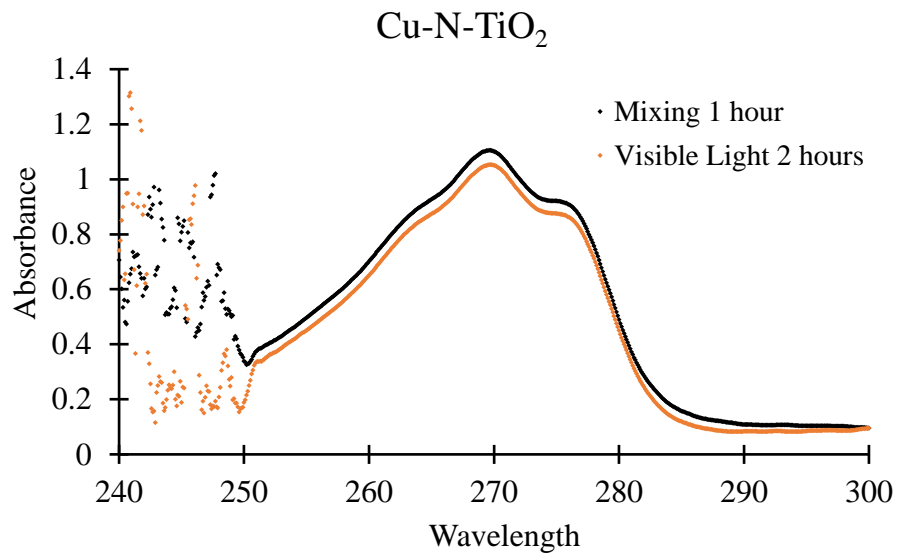


Figure 13. The UV-Vis Absorbance Spectra using the Cu-N-TiO_2 Catalyst in the Visible Spectrum (2-hour irradiation period).

UV Light Conditions

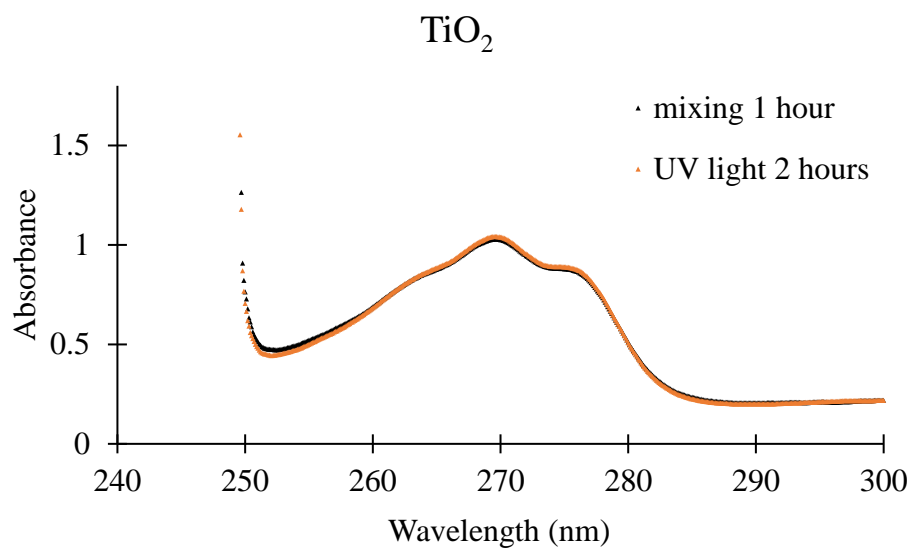


Figure 14. The UV-Vis Absorbance Spectra using the TiO_2 Catalyst in the UV Spectrum (2-hour irradiation period).

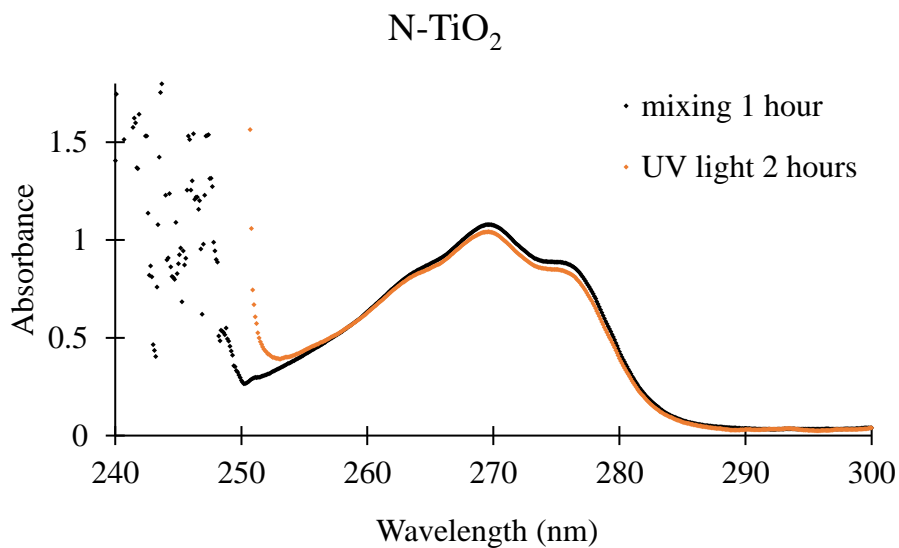


Figure 15. The UV-Vis Absorbance Spectra using the N-TiO_2 Catalyst in the UV Spectrum (2-hour irradiation period).

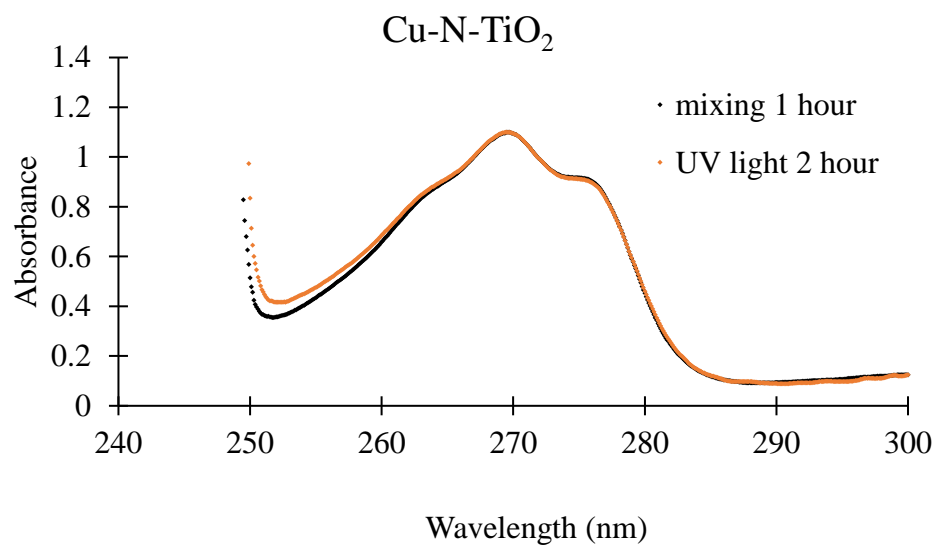


Figure 16. The UV-Vis Absorbance Spectra using the Cu-N-TiO₂ Catalyst in the UV Spectrum (2-hour irradiation period).