

In-depth Study of Trichloroethylene Photodegradation by Titanium Dioxide Nanoparticles: Anatase versus Brookite

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Abstract

Trichloroethylene, TCE, is a volatile industrial solvent that has been identified as a human carcinogen and contaminant by the US EPA. Titanium dioxide, TiO_2 , is a widely available environmental photocatalyst that is able to degrade volatile organic contaminants under UV light. TiO_2 is capable of crystallizing in three polymorphic structures: anatase, rutile, and brookite. Brookite TiO_2 is highly under researched and shows potential as an effective photocatalyst. In this study, a detailed comparison of purchased and synthesized Brookite, Brookite-Rich, Anatase, and Anatase-Rich NPs was conducted to determine effectiveness in the photodegradation of TCE. Photocatalysis of aqueous solutions containing TCE and TiO_2 NPs were exposed to UV-light and analyzed with GC-MS at desired minute intervals in accordance with EPA methods. Samples were run in neutral, acidic, and alkaline conditions. In all alkaline conditions no changes to the degradation rate of TCE were experienced. In neutral conditions purchased Anatase and Brookite had comparable activity both degrading TCE effectively. Purchased and synthesized Anatase-Rich NPs performed worse than purchased Anatase. Purchased anatase and synthesized anatase performed similarly in TCE degradation, both degrading 80% of TCE in 3 mins of UV. Brookite-rich degraded 90% of TCE in 2 mins of UV exposure increasing the photocatalytic efficiencies of purchased NPs. Purchased Brookite-Rich outperformed all five: purchased Brookite, synthesized Brookite-Rich, Anatase, purchased and synthesized Anatase-Rich. Purchased brookite degraded 85% of TCE in 3 mins of UV whereas, synthesized

brookite degraded 99% of TCE in 1 min of UV. Synthesized Brookite had a significant increase in rate of degradation, outperforming every other sample. Basic conditions did not increase degradation rate of TCE and extreme acidic pH increased TCE degradation with and without purchased brookite NPs. The results of this project provide evidence towards the optimal conditions for the photodegradation of TCE with TiO_2 NPs.

1. Introduction

Industrial waste poses a real issue in today's society. Improper waste disposal of many industrial solvents has allowed volatile organic compounds, VOCs, to get trapped in the nation's groundwater posing a threat not just to the nation's drinking supply but the surrounding environments as well. VOCs are known for evaporating quickly in the exposure to air.¹ However, once trapped underground in the groundwater they cannot evaporate and instead are deposited into nearby bodies of water and streams. The focus of this study is on the VOC, Trichloroethylene or TCE. TCE is estimated to be in 34% of the nation's drinking supply, with a maximum contaminant level set at 5 ppb. TCE is a dense non-aqueous phase liquid with a high density of 1.465 g/ml, and a low solubility in water.² These qualities make it difficult to remove TCE from water once dissolved into groundwater. TCE was chemically synthesized and used as an analgesic during the 1940s-1950s, but was banned from medical use by the FDA in the late 1970s.³ TCE is used in household cleaners, spray adhesives, and as an industrial solvent for degreasing metals prior to electroplating.⁴ The waste from the sites that produce TCE are polluting the surrounding environment and pose hazards to the health of the surrounding communities. TCE has been identified as a human carcinogen and contaminant by the US EPA.⁵ TCE's health effects can be caused from inhalation as well as consumption. Inhalation can cause adverse health effects that primarily affect the Central Nervous System such as: dizziness, headache, sleepiness, nausea, confusion, blurred vision, facial numbness, and weakness.⁶ The health effects from consumption range from effects on the liver, kidneys, immune and endocrine systems.⁶ On top of these previously stated health effects from TCE, as a carcinogen and prolonged exposure to TCE can cause kidney cancer.⁴ Research to find an effective non-toxic method to purify this chemical is necessary.

Titanium dioxide, TiO_2 , is a widely available, cost effective, and non-toxic material that in the nano size regime can be used as an optimal filtration medium.⁷ This is due to its photocatalytic characteristics in the presence of organic contaminants and ultraviolet light in the process known as photocatalytic oxidation, PCO. The discovery was made by Fujishima and Honda in 1972 with the development of a successful method in electrochemical photolysis of water at a semiconductor electrode, in this case TiO_2 .⁸ PCO is successful in the removal of toxins in water and air. The PCO process is able to break down these VOCs in solutions under UV light without any other additive utilizing only TiO_2 as a catalyst. When the catalyst, in our case TiO_2 , is exposed to the sun, the UV light in the presence of water vapor allows for hydroxyl radicals, and superoxide anions, two highly reactive substances to be formed. This formation of radicals is a result of the excitation of electrons in the valence band to the conduction band creating electron hole pairing. Simultaneous oxidation and reduction then begin with these

radicals allowing for the airborne VOC, in our case TCE, to be able to break down into nonhazardous molecules like CO_2 , O_2 , H_2O , and other intermediates. This entire process is shown in Figure 1.

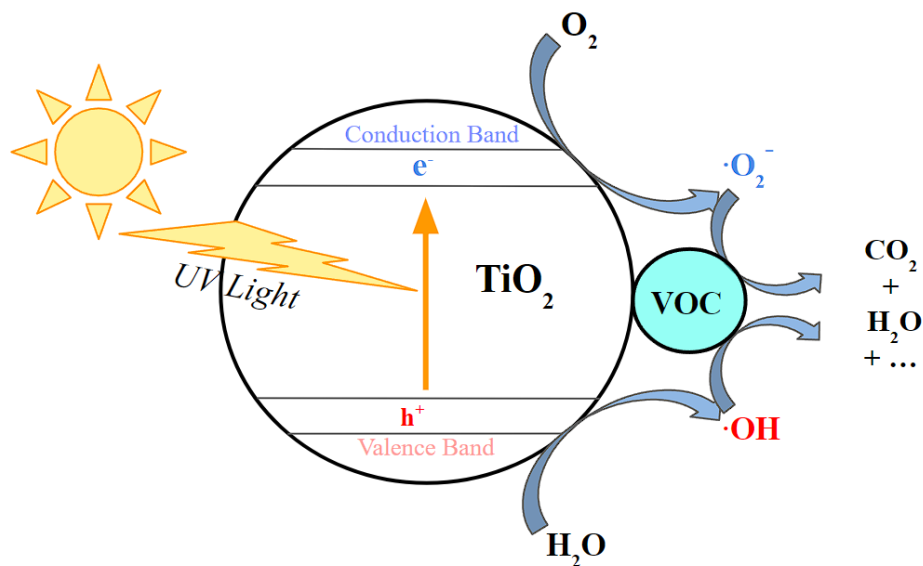


Figure 1. PCO mechanism utilizing TiO_2 under UV light as a catalyst to break down a VOC into intermediates.

TiO_2 NPs are capable of three polymorphic structures: anatase, rutile, and brookite. Anatase and rutile are both tetragonal in shape, they possess three perpendicular axes with two of the same length and one in varying length. Brookite is orthorhombic meaning that all three of brookite's perpendicular axes are of varying lengths. The dimensionality of these structures determines the properties exhibited by the NPs. There are physical properties including surface area and adsorption as well as electronic properties which include: band gap, charge carrier lifetime, electron mobility, trapping sites, surface energetics, surface atom arrangements, and adsorption sites.⁹ All of the properties exhibited have an influence on the NPs photocatalytic performance as well. Of these three crystal polymorphs of TiO_2 , brookite presents the most undiscovered potential. This is due to its novelty in research, newer methods of facile synthesis, and unique orthorhombic structure.¹⁰ Brookite TiO_2 was once regarded to not be suitable as a photocatalyst due to complications in synthesizing a stable version.⁹⁻¹² However, later successful synthesis of nanostructured brookite through multiple different methods were shown to greatly enhance the photocatalytic performance of the NPs.⁹ Now it is theorized that brookite may have higher photocatalytic activity based on the optimized qualities of the structure. Brookite's potential as a catalyst lies within the crystallinity and higher specific surface area which provides brookite with the potential to be more reactive than anatase.¹² The increase of specific surface area results in more active sites in the PCO process. Depth of charge carrier trapping greatly affects the photocatalytic activity of the NPs. Brookite's unique structure traps electrons in shallow traps and not photogeneration, extending the lifespan of the hole and reduces the free electron amount present.¹³

The electron hole recombination occurring within the NPs is a driving force behind PCO and the energy required determines the effectiveness of the NP. Anatase is found to have a band gap energy of 3.2 eV, a lower potential energy than that of brookite. Brookite is capable of having a range of band gaps between the energies of 3.0-3.4eV.⁷ This allows for further exploration into adjusting brookite band gap through synthesis to achieve different levels of PCO. The effectiveness of each structure is argued by different studies which is why this comparison of brookite and anatase is needed. A study by Li, J. et al. investigated synthesizing pure phase rutile, anatase, and brookite TiO₂ and determined that the synthesized brookite NPs, with an optical band gap of 3.11 eV and the indirect band gap of 2.85 eV, had the highest photocatalytic efficiency.¹⁴ A study by Kandiel, T. et al. suggests that pure brookite nanoparticles exhibit a higher photocatalytic activity than brookite-rich nanoparticles and anatase nanoparticles.¹⁵ The electron band gap also greatly affects the effectiveness of PCO performance. A study by Koelsch et al. determined the band gap of brookite nanoparticles as 3.4 eV, they found this through measuring the optical transmission of brookite dispersions at different concentrations and by UV fluorescence measurements.⁷ Further comparisons on brookite and anatase's different band gaps and energy required for electron hole recombination can aid in discovering the most effective catalyst out of the two.

In addition to comparing anatase to brookite in effectiveness, further studies are being reported on the improved properties of phase mixtures. Instead of heterogeneous pure phase brookite or anatase, studies similar to that of Zaho, H. et al. look into mixtures of anatase-rich or brookite-rich NPs. The study done by Zhao, H. et al. compared a bicrystalline anatase-rich/brookite mixture with a 75:25 ratio that proved to be more active for photodegradation than Degussa P25, an anatase-rich/rutile mixture with a 75:25 ratio, as well as single phase anatase and brookite.¹⁶ The review by Monai M. concludes that the results of Zhao's study suggests that more research could be done in investigation the electron transfer that may take place in brookite-based TiO₂ composites.⁹ This increased rate of degradation witness can be from the junction between the conduction bands of the catalysts that are able to promote longer hole life and differ electron hole recombination.

Another method of improving degradation of contaminants using photodegradation is through altering pH. Using acidic environmental conditions allows for increased reactive oxygen species formation throughout the aqueous sample, further promoting PCO. A pH investigation was done by Ndong, et. al. where they tested TCE degradation in acidic, neutral, and basic conditions using anatase nanosheets as the catalyst.²⁰ The effects of pH on TCE degradation were negligible because complete degradation occurred in all the tested pH solutions that used the anatase TiO₂. However, not many studies have been done investigating the pH effect on PCO utilizing brookite NPs as the catalyst, which is why it was decided to pursue this question.

The overall goal of this experiment is to achieve a detailed comparison of the photodegradation of TCE utilizing the brookite and anatase TiO₂ NPs to determine which structure is optimal. In this study purchased and synthesized TiO₂ NPs as well as mixtures of anatase-rich and brookite-rich will be compared. Using Gas Chromatography and Mass Spectrometry (GC/MS) partnered with a Purge and Trap aqueous samples of known TCE concentrations and TiO₂ NPs were analyzed. Solutions of TCE mixed with NPs are exposed to UV light in a photoreactor and extracted at known intervals of time to test with the GC-MS. Through this process determining the percent of degradation TCE experiences coupled with each NP will allow for the comparison of anatase and brookite efficiencies.

2. Materials and Experimental Methods

2.1. Safety Data and Materials

Trichloroethylene's CAS Number is 79-01-6 and considered to be an irritant and a health hazard.¹⁸ Hazard statements include the following: causes skin irritation, causes serious eye irritation, may cause an allergic skin reaction, may cause drowsiness or dizziness, suspected of causing genetic defects, may cause cancer, and may cause damage to organs through prolonged or repeated exposure.¹⁸ TCE is acutely toxic and a known human carcinogen.¹⁸ **Caution!** TCE is a GHS category 2 in skin irritancy, a category 2A eye irritancy, a category 1 skin sensitization, category 2 germ cell mutagenicity, a category 1B carcinogenicity.¹⁸ **Caution for single and short-term exposure!** TCE is a GHS category 3 in specific target organ toxicity, and central nervous system, and a category 3 aquatic hazard.¹⁸ **Caution for long-term exposure!** TCE is an aquatic hazard GHS category 3.¹⁸ For safe handling TCE was used under a fume hood in small amounts to avoid inhalation of vapors, while using personal protective equipment. For safe storing any glass vial containing TCE was tightly sealed and wrapped in parafilm then placed in the fridge to prevent evaporation.

Brookite TiO₂ nanopowder, <100 nm, 99.99% trace metals basis was purchased from Sigma Aldrich. Anatase TiO₂ nanopowder, <25 nm particle size, 99.7% trace metals basis was purchased from Sigma Aldrich. Both brookite, CAS number 12188-41-9, and anatase, CAS number 1317-70-0, are non-hazardous materials. When handling the nanopowders safety precautions such as trying not to disturb the powder were taken to avoid inhalation. For safe storing nanopowders were kept out of sunlight and in the fridge in glass vials.

2.2. Calibration Curve

The samples were run in accordance with the EPA standard, method 524.2. Samples were analyzed using a Shimadzu GC/MS QP2010 Plus with a Restek Rtx-624 column and a Teledyne Tekmar Stratum Purge and Trap. To create the calibration curve first each sample run contained 5 mL of ultrapure deionized water and 10 µL of 15 ppm internal standard. 1,4-Difluorobenzene is the consistent internal standard used as a reference to track the area of TCE with a retention time of around 10.5 min and a mass of 114 g/mol. Conveniently, TCE is present at a retention time of 10.8 min with a mass of 95 g/mol making 1,4-difluorobenzene a good reference to build the calibration curve.

The only change was the varying concentrations of VOC mix, specifically TCE, which were added ranging from 5 ppb to 50 ppb. The 5mL aqueous samples were inserted into the Purge and Trap, where the sample was purged with inert gas causing the sample to bubble and release the volatile gases into the GC/MS.

2.3. Photocatalysis

Photocatalysis was performed under 240 nm UV light in the Rayonet Reactor with 12W per lamp. The aqueous solutions were analyzed at desired illumination intervals (~0, 30, 60, 90, 120 sec). For the photocatalysis 2 mg of purchased NPs were added to a 45 mL vial with a known concentration of TCE (~60 ppb). Each vial was wrapped in foil and stored in the fridge overnight to set to equilibrium, allowing for the adsorption and desorption to settle. The next day, after 5 mins of sonication, the solution was transferred into a quartz test tube with a lid and photocatalyzed. Then 5mL of that solution was analyzed with 10 μ L of 15 ppm internal standard. Using the equation from the calibration curve the concentrations of TCE were calculated. Each sample was tested on at least three different days and averaged in order to show the general trend.

2.4. Brookite-Rich and Anatase-Rich

Brookite-Rich and Anatase-Rich samples were created using the purchased brookite and anatase NPs. For 2mg of NPs the ratio of 75%-25% was used by weight. The rest of the preparation and testing followed the same protocol as stated in section 2.3.

2.5. Acidic and Alkaline Conditions

The comparison of Acidic and Alkaline conditions effects of photodegradation was conducted using the same preparation in section 3.2. After obtaining the 45mL vials with 2mg of NPs, the pH was altered using drops of Nitric Acid, HNO_3 , to make the solution acidic and Sodium Hydroxide, NaOH , to make the solution basic. Additional acidic conditions were created using Sulfuric acid, Confirming the pH with pH test strips, a wide array of pHs were created ranging from 1 to 13. The experimental method proceeds as normal to test and collect the data as shown in section 2.3.

2.6. Synthesized Brookite & Anatase

Brookite and anatase NPs were synthesized by group member who followed previously reported work.¹⁹

3. Results and Discussion

3.1. Calibration Curve Data

The calibration curve created for the ratio of TCE/IS vs. TCE Concentration (ppb) is seen in Figure 2. By taking the ratio of the internal standard and VOC areas and plotting them as the y axis and the x-axis of concentrations ranging from 5 to 50 ppb the calibration curve in Figure 2 was produced. The calibration curve possessed an R^2 value of 0.987 with a limit of detection, LOD, of 7.63 ppb and a limit of quantification, LOQ, of 23.12 ppb.

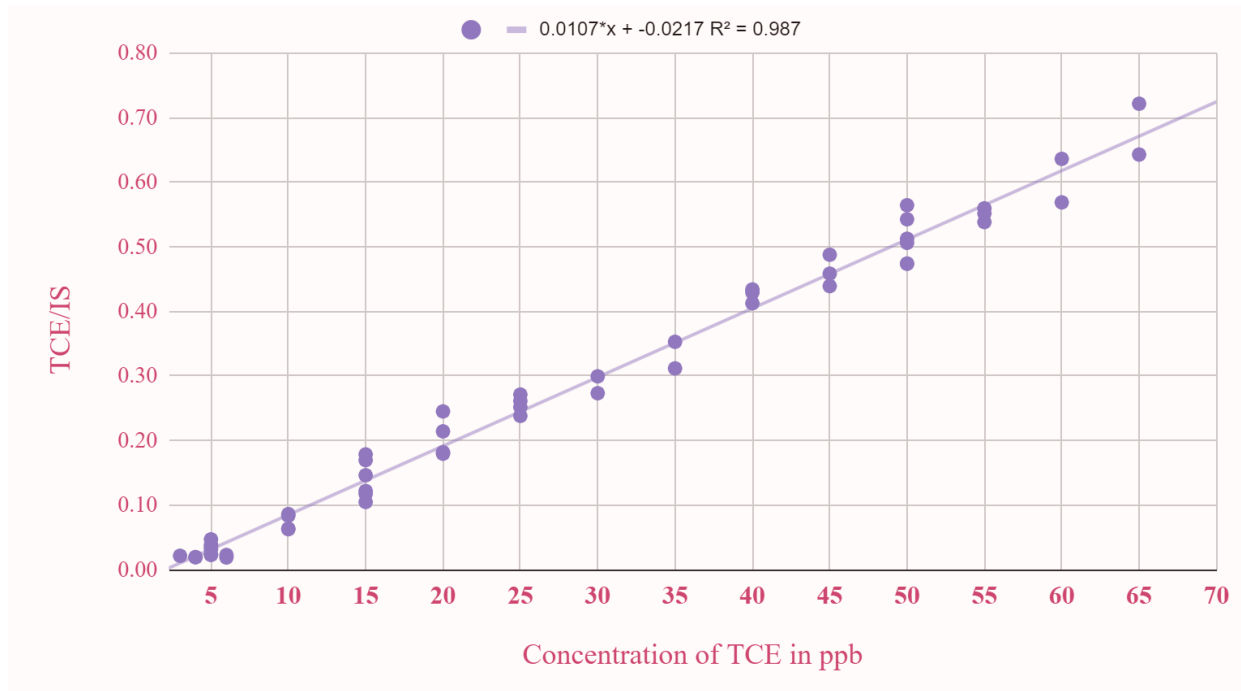


Figure 2. Calibration Curve of TCE/IS vs. TCE Concentration (ppb)

3.2. TCE Degradation by UV Only

To begin the photodegradation tests, first a control test of TCE in the absence of NPs was conducted. The solution of TCE was run in minute intervals of UV exposure from 0 to 3 minutes and the results are shown in Figure 3. Three samples were tested and averaged to show the overall trend of the data as well as show reproducibility. After 3 mins of UV exposure the sample experienced roughly 34% of degradation. Degradation is commonly seen with TCE alone in exposure to UV light. This amount is negligible and commonly is limited, this is seen in Cho's study on TCE degradation where under solar irradiation TCE degrades to only 85% concentration in 6 hours of exposure¹⁷.

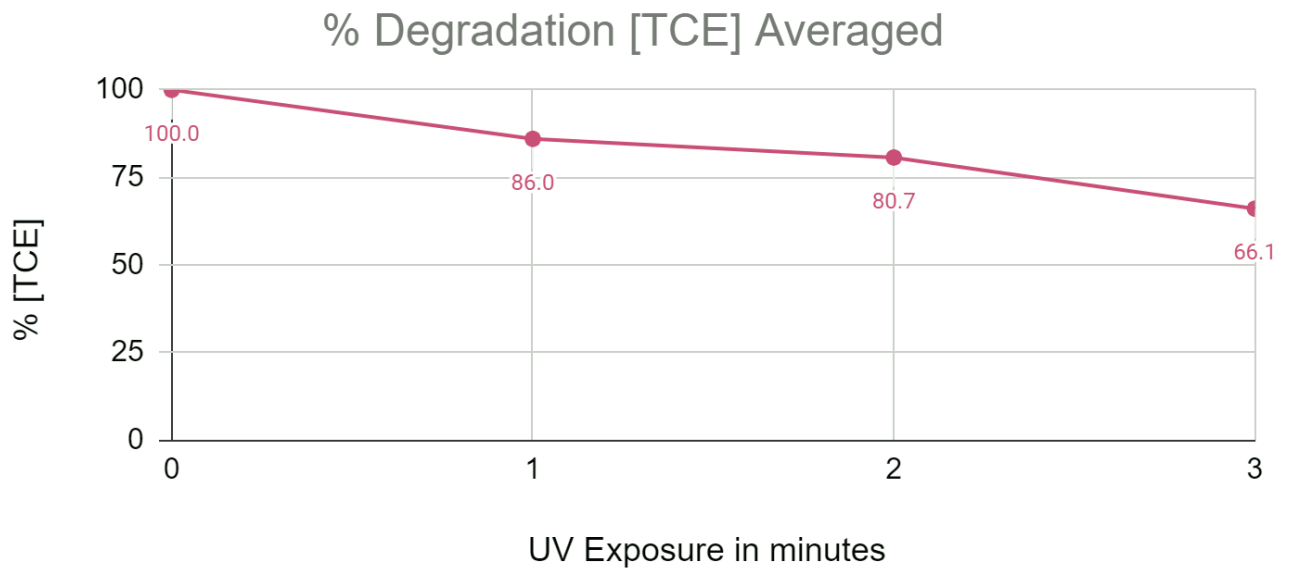


Figure 3. The average percent degradation of TCE concentration in the absence of any NPs over 3 minutes of UV exposure.

3.3. Anatase NPs characterization

SEM images of purchased anatase NPs and synthesized anatase NPs were taken with a JEOL JSM-IT700HR SEM Scanning Electron Microscope and shown in Figure 4, with a 100nm scale bar. The purchased anatase NPs were spherical in shape with an estimated size of L: 15-50 nm and W: 10-25 nm. The synthesized anatase NPs were cylindrical in shape and smaller in size than the purchased NPs. Synthesized anatase NPs had an estimated size of Length: 50-80 nm and Width: 10-25 nm.

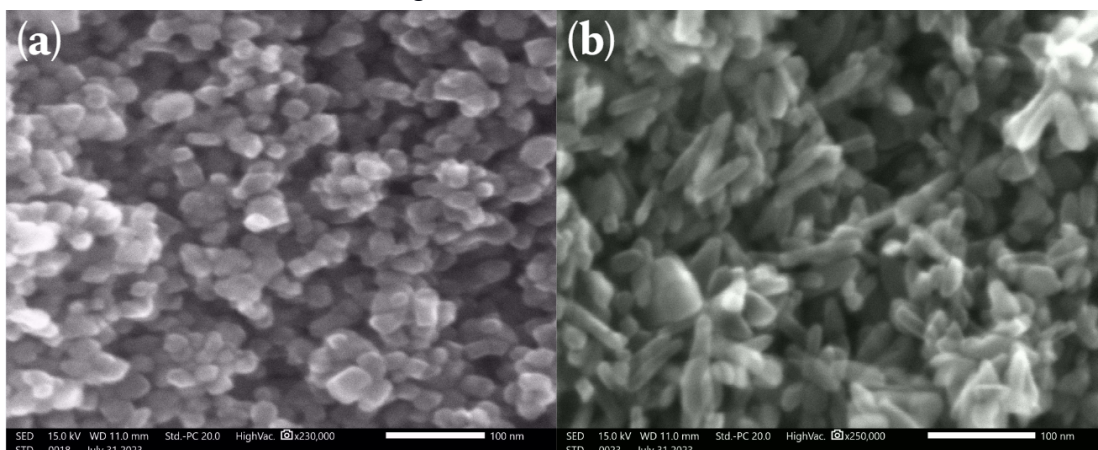


Figure 4. SEM Images (a) purchased anatase NPs and (b) synthesized anatase NPs.

3.4. Photodegradation of TCE by purchased anatase NPs vs synthesized anatase NPs.

The averaged results of the multiple tests ran with the 2 mg of purchased and synthesized anatase NPs are shown in Figure 5. Purchased anatase NPs and synthesized anatase NPs were both tested on separate occasions to prove reproducibility and averaged. After one minute of UV exposure the purchased anatase was able to degrade TCE concentration to 52% and after 3 minutes the sample contained only 17% concentration of TCE remaining. The concentration of the final sample taken at 3 minutes was still above the max contamination level of 5 ppb. The synthesized anatase NPs had a similar degradation rate as the purchased anatase NPs. In one minute of UV illumination, they degraded TCE to roughly 50% and 3 minutes to about 15% concentration of TCE remaining in the sample.

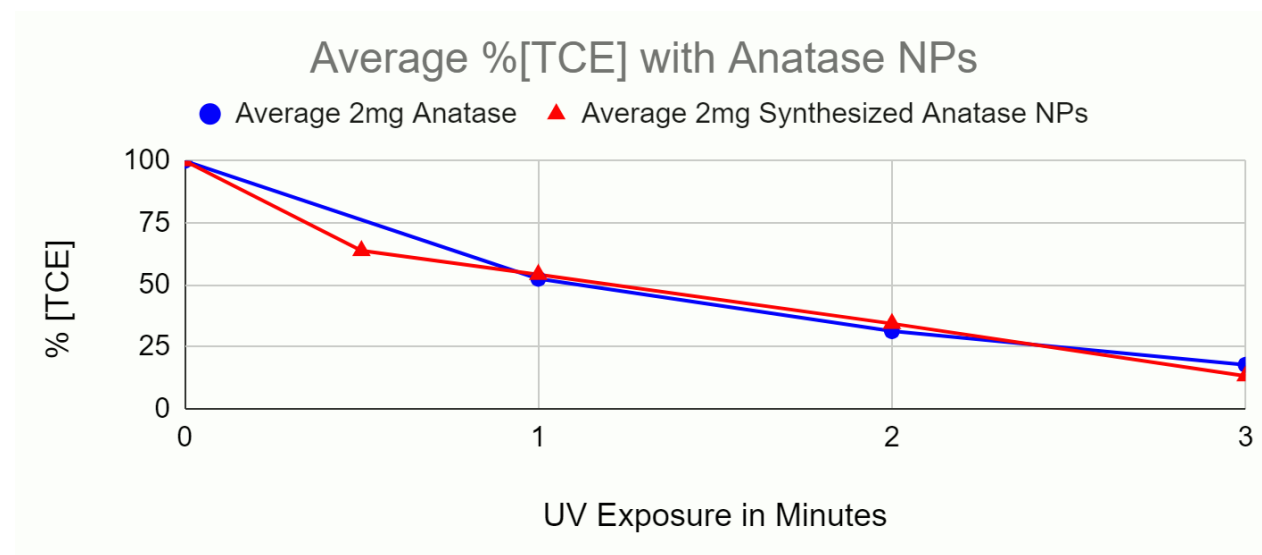


Figure 5. The comparison of averaged percent degradation of TCE concentration by purchased anatase NPs (blue circle) and synthesized anatase NPs (red triangle).

3.5. Photodegradation of TCE by purchased anatase-rich NPs vs synthesized anatase-rich NPs.

The comparison of purchased anatase-rich and synthesized anatase-rich NPs on the photodegradation of TCE is shown in Figure 6. The purchased anatase-rich and synthesized anatase-rich NPs were both tested on two separate occasions to prove reproducibility and averaged. Both performed similarly in degradation of TCE. After 3 minutes of UV illumination both samples were down to about 22% concentration of TCE remaining. Anatase-rich NPs both synthesized and purchased did not outperform purchased anatase in the degradation of TCE, this comparison is shown in figure 10.

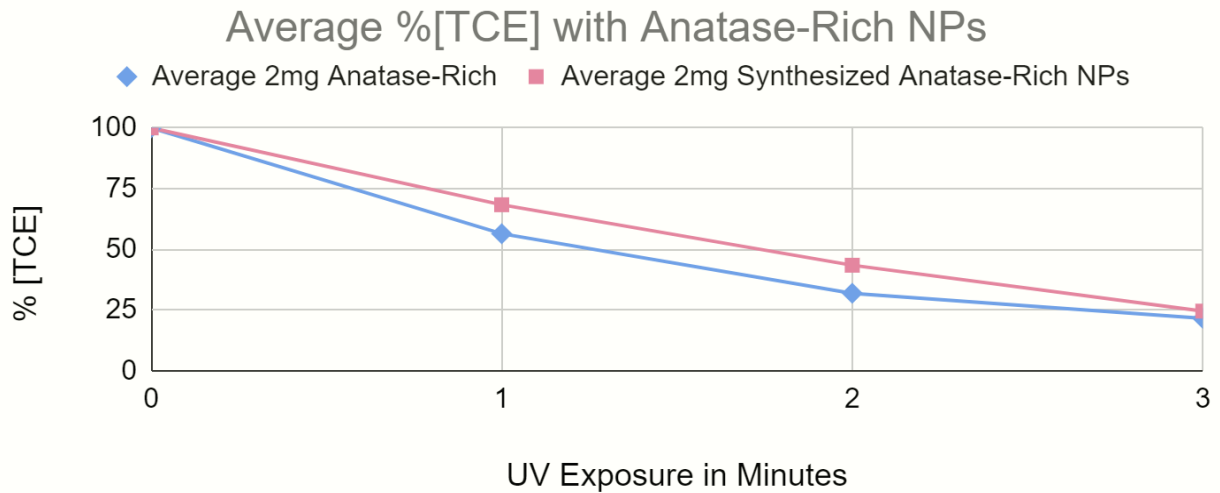


Figure 6. The comparison of averaged percent degradation of TCE concentration by of purchased anatase-rich NPs (light blue diamond) and of synthesized anatase-rich NPs (light pink square).

3.6. Brookite NP Characterization

SEM images of purchased brookite NPs and synthesized brookite NPs are shown in Figure 7, taken with the 200nm scale bar. The purchased brookite NPs are spherical and interconnected in a large crystal structure. The purchased NPs have an estimated size of L: 50-120 nm and W: 25-80 nm. The synthesized brookite NPs were larger, elongated, and less interconnected than the purchased brookite NPs. The synthesized NPs have an estimated size of Length: 100-500 nm and Width: 25-100 nm.

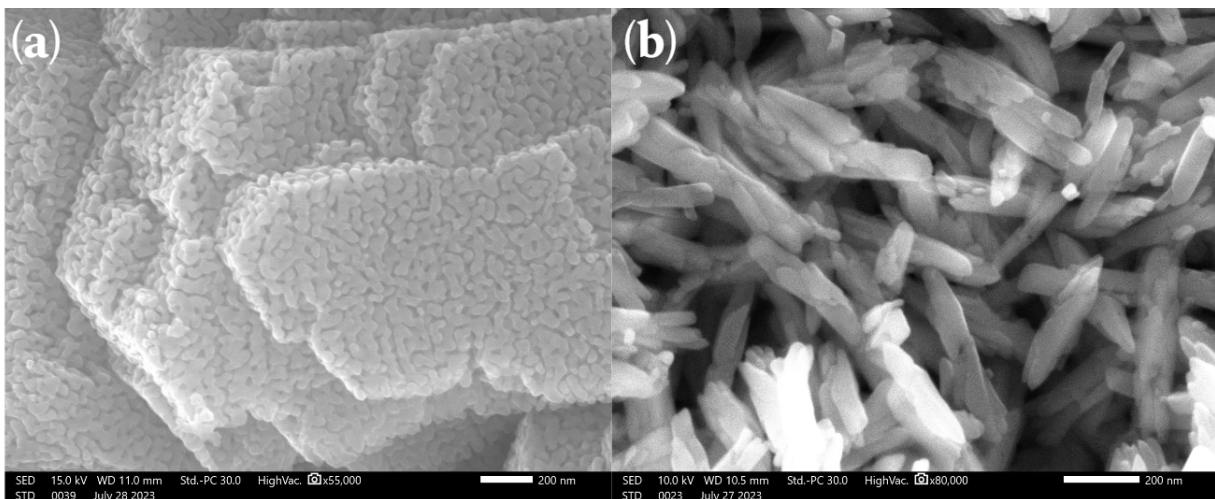


Figure 7. SEM Images (a) purchased brookite NPs and (b) synthesized brookite NPs.

3.7. Photodegradation of TCE by purchased brookite NPs vs synthesized brookite NPs.

The averaged results of the multiple tests ran with the purchased and synthesized brookite NPs are shown in Figure 8 to get the overall trend of effect on TCE degradation. After one minute of UV exposure the purchased brookite NPs degraded 50% of TCE and down to 25% of TCE concentration remaining in two minutes. After 3 minutes of UV exposure the purchased brookite NPs were able to degrade TCE by 88%. Synthesized brookite NPs experienced a much faster rate of TCE degradation. In just one minute of UV exposure almost all of the TCE was degraded from the samples. The synthesized brookite NPs were able to degrade TCE to under the max contamination level of 5 ppb in one minute of UV exposure.

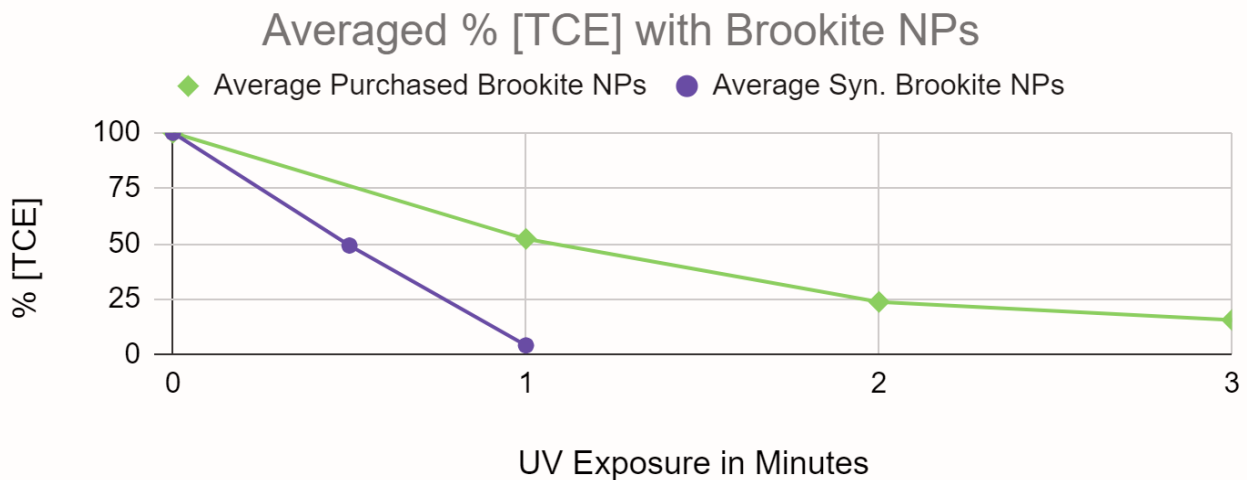


Figure 8. The comparison of averaged percent degradation of TCE concentration by purchased brookite NPs (light green diamond) and synthesized brookite NPs (purple circle).

3.8. Photodegradation of TCE by purchased brookite-rich NPs vs synthesized brookite-rich NPs.

The comparison of purchased brookite-rich and synthesized brookite-rich NPs in the average percent concentration of TCE degradation is shown in Figure 9. Purchased brookite-rich NPs and synthesized brookite-rich NPs were both tested on at least two separate occasions to prove reproducibility and averaged. Both improved the rate of degradation of TCE in comparison to regularly purchased brookite (Figure 10). Specifically purchased brookite-rich NPs showed an increase in degradation rate in comparison to purchased brookite. TCE was completely degraded from the samples with purchased brookite-rich NPs in 2 minutes of UV exposure and outperformed synthesized brookite-rich NPs. This result shows that you can improve the rate of degradation using purchased NPs and a specific mixing ratio.

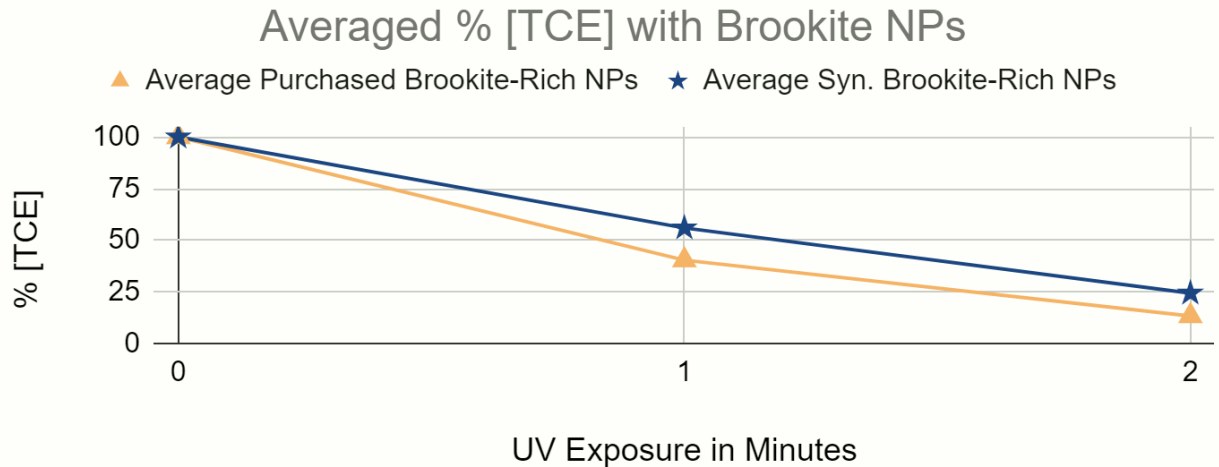


Figure 9. The comparison of averaged percent degradation of TCE concentration by purchased brookite-rich NPs (orange triangles) and synthesized brookite-rich NPs (dark blue stars).

3.5 Comparison of Brookite vs Anatase in the photodegradation of TCE: Synthesized NPs, Rich NPs, and Purchased NPs

When comparing brookite and anatase NPs conditions were kept as similar as possible and with the same concentration of TCE. The results for all purchased NPs in the degradation of TCE were averaged and graphed in percent concentration of TCE in Figure 10. Both purchased brookite and anatase NPs were comparable in effectiveness in degrading TCE. Anatase-rich NPs slightly decreased the degradation rate. Brookite-rich NPs experienced a significant increase in degradation of TCE with only 2 minutes of UV exposure; the sample degraded the TCE to under the max contamination level of 5 ppb. These results show that the most favored purchased combination of NPs would be a ratio of 75% brookite to 25% anatase TiO₂ NPs.

The results for all synthesized NPs in the degradation of TCE were averaged and graphed in percent concentration of TCE in figure 11. All three: anatase, anatase-rich, and brookite-rich NPs had comparable degradation rates of TCE. The most effective in TCE degradation would be synthesized brookite NPs. These NPs outperformed all samples tested and were able to degrade TCE under max contamination of 5 ppb in only 1 minute of UV illumination.

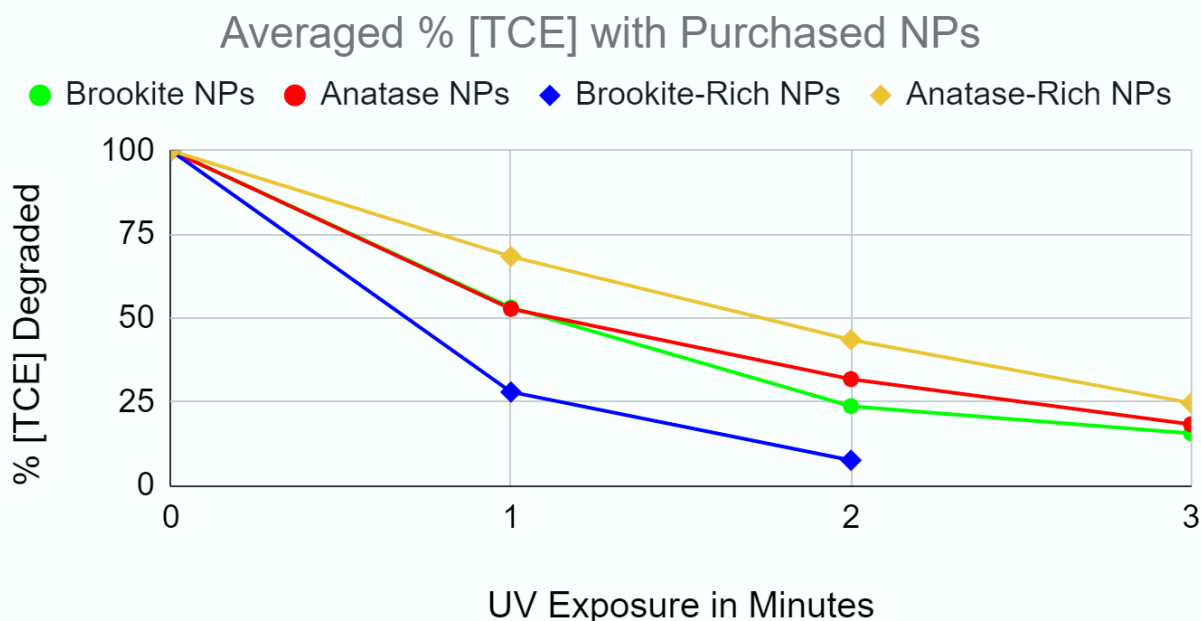


Figure 10. The comparison of averaged percent degradation of TCE concentration by purchased anatase NPs (red circle), purchased brookite NPs (green circle), purchased anatase-rich NPs (yellow diamonds), and purchased brookite-rich NPs (blue diamond).

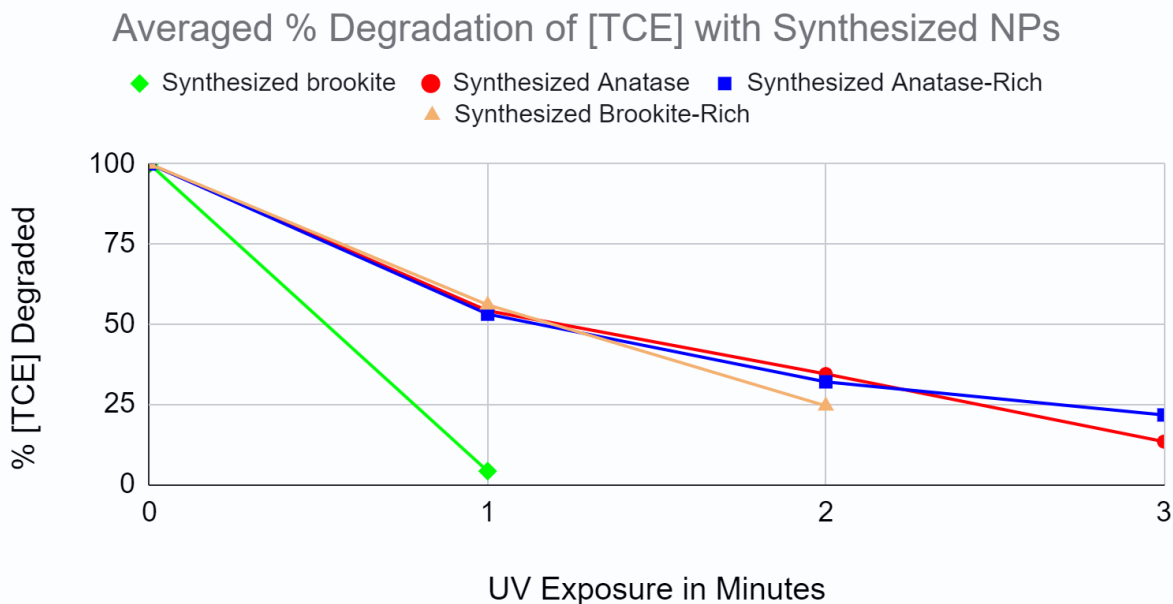


Figure 11. The comparison of averaged percent degradation of TCE concentration by synthesized anatase NPs (red circle), synthesized brookite NPs (green diamond), synthesized anatase-rich NPs (blue squares), and synthesized brookite-rich NPs (orange triangle).

3.5. Neutral, Acidic, and Alkaline Conditions

All acidic conditions were run at a pH of 1 and 3, then averaged to generate a general trend. All basic conditions were run at a pH of 10 and 13, then averaged as well. The comparison of average percent concentration of TCE in acidic, basic, and neutral conditions in the absence of NPs is shown in Figure 12. To adjust the pH nitric acid and sodium hydroxide were added to the solutions.

Nitric acid is a strong acid that ionizes into hydronium and nitrate ions in aqueous solutions.²¹ Also, nitric acid is a powerful oxidizing agent that acts as an electron acceptor in oxidation-reduction reactions commonly seen in PCO.²¹ Keeping that in mind it was not surprising that nitric acid without any NPs was capable of completely degrading TCE with exposure to UV light. This occurred in under a minute of UV exposure and resulted in an end concentration under that of the max contamination level of 5 ppb. This was not a surprising result since nitric acid is known to be a strong oxidizer and it can decompose organic matter. When NPs were added that same trend with nitric acid was present in each sample. To observe degradation of TCE in acidic conditions with different acids, sulfuric acid was used to set solution to pH 3. When TCE alone devoid of any NPs was exposed to UV light with sulfuric acid, no extra degradation was seen. Even when tested with NPs the average trend of degradation was not affected by the addition of sulfuric acid (Figure 13). This preliminary data will be researched in more detail in the future.

All basic conditions observed not to have any large change in degradation rate of TCE. This was hypothesized for a basic environment that could prevent PCO from occurring. Studies that compare pH also confirmed that basic conditions either decrease or have no effect on degradation of contaminants with and without NPs. Basic conditions were an average of pH 10 and 13 tests. The results without NPs can be seen in Figure 12 and the results with purchased brookite NPs can be seen in Figure 13.

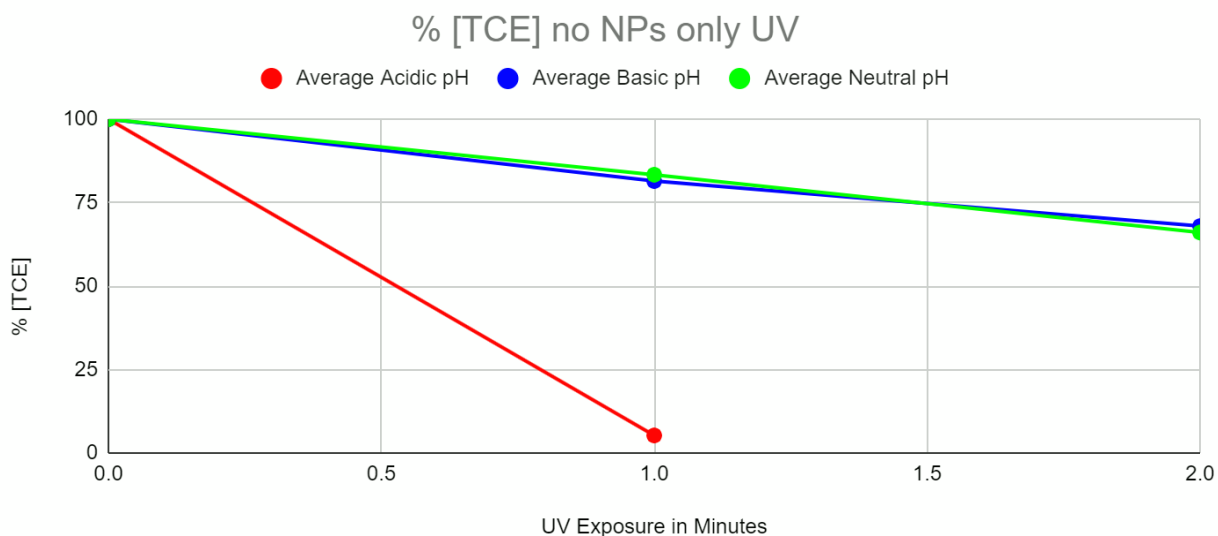


Figure 12. Average percent degradation of TCE in neutral, acidic, and basic conditions with no NPs, only UV illumination. Nitric acid (red circle), sulfuric acid (yellow circle), and neutral (green circle).

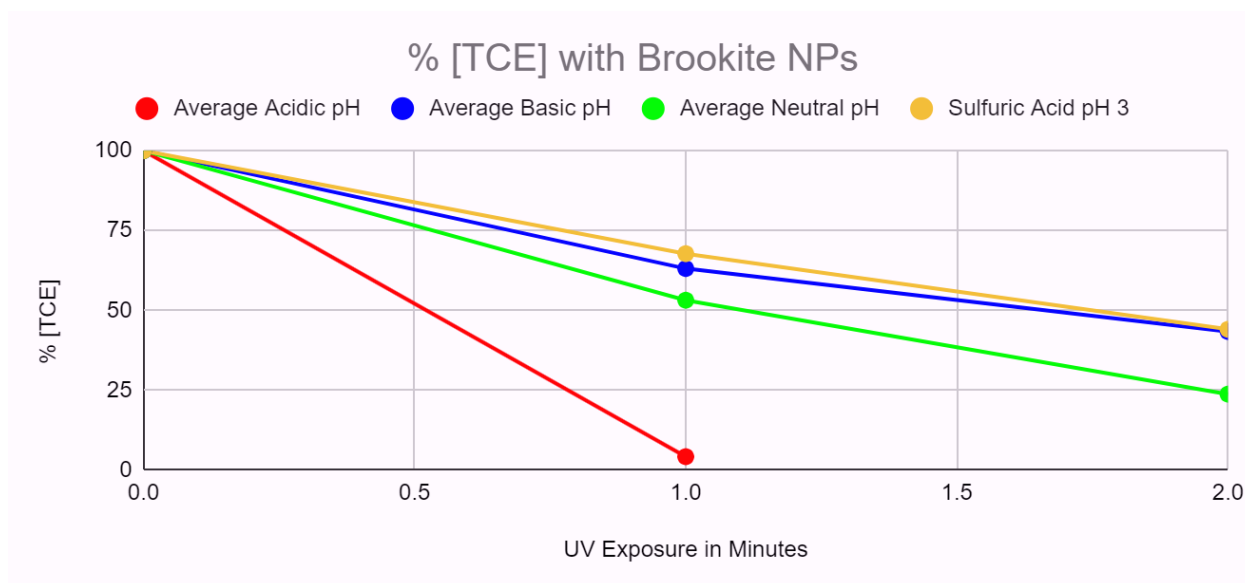


Figure 13. Average percent degradation of TCE in neutral, acidic, and basic Conditions with purchased brookite NPs and UV illumination. Nitric acid (red circle), and sulfuric acid (yellow circle), neutral (green circle), and Sodium Hydroxide (blue circle).

4. Conclusion

The overall results show the varying efficiencies in TCE degradation that purchased and synthesized TiO_2 NPs are capable of. The comparison between anatase, anatase-rich, brookite, and brookite-rich NPs were done for purchased and synthesized NPs to determine the most effective photocatalyst. Purchased anatase and synthesized anatase performed similarly in TCE degradation, both degrading 80% of TCE in 3 mins of UV. Purchased brookite degraded 85% of TCE in 3 mins of UV whereas, synthesized brookite degraded 99% of TCE in 1 min of UV. Synthesized brookite NPs were concluded to be most effective for its large increase in the rate of degradation out of all tests. Out of all the purchased NPs, brookite-rich NPs showed the most effective degradation rate of TCE. Brookite-rich degraded 90% of TCE in 2 mins of UV exposure increasing the photocatalytic efficiencies of purchased NPs. This confirms that the junction between brookite and anatase allowed for the continuation of PCO and extended electron hole recombination. Extreme Acidic pH increased TCE degradation with and without purchased brookite NPs. Basic conditions did not increase degradation rate of TCE; however more in-depth studies need to occur, specifically in acidic conditions.

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