

pH Effect on Photocatalytic Degradation of Trichloroethylene by Brookite Titanium Dioxide Nanoparticles

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Abstract

Trichloroethylene (TCE) contamination of ground and surface waters presents many adverse health risks. It is expensive and difficult to remove TCE and other volatile organic pollutants from contaminated water efficiently and large-scale. Photochemical processes such as UV coupled with titanium dioxide nanoparticles have gained popularity in recent decades, offering promising methods of removing volatile organic compounds such as TCE from contaminated sources. Titanium dioxide exists in three crystal phases: anatase, rutile, and brookite, as well as in combinations of the three. While anatase and rutile are extensively studied photocatalysts, the photocatalytic potential of brookite is largely undocumented in literature. This study observes the degradation of TCE in the presence of brookite with UV irradiation using Gas Chromatography Mass Spectroscopy over various time intervals. The relationship between pH and the rate of degradation of TCE in the presence of brookite is also explored. The pH of solution affects many factors, such as the electrostatic interactions occurring on the catalytic brookite surface, solvent molecules, and charged radicals formed during the degradation of TCE. This experiment investigates the pH effect by comparing the degradation rate of TCE in highly acidic and basic aqueous solutions and analyzing data from photodegradation trials to find the optimal conditions for the photocatalytic degradation of TCE with brookite titanium dioxide nanoparticles. Experiments conducted in basic conditions demonstrated a higher rate of degradation of TCE with brookite, while experiments in highly acidic conditions showed a higher rate of degradation of TCE in the absence of brookite.

1. Introduction

Trichloroethylene (TCE) is a colorless volatile organic compound (VOC) historically used as a solvent and degreaser, found to contaminate ground and surface waters. The presence of TCE in water sources is concerning due to its cytotoxicity, environmental persistence, carcinogenic effects, and toxic intermediates such as cis-1,2-dichloroethylene, vinyl chloride, 1,1-dichloroethane, chloroethane, and 1,1-dichloroethylene, formed through hydrogenolysis due to long-term microbial dechlorination.¹ A risk assessment performed by the U.S. Environmental

Protection Agency (EPA) found both short and long-term effects from exposure to TCE. Prolonged exposure has been associated with damage to the liver, kidneys, immune system, as well as damage to the central nervous system.² Although TCE exposure typically occurs through inhalation in industrial settings, it is harmful through all routes of exposure, including through skin and through ingestion. Out of the fifty-four conditions of use for TCE, the EPA found that fifty-two conditions of use present unreasonable risks to human health.³ The EPA has the maximum contaminant level of TCE in drinking water at 0.005 mg/L, or five parts per billion (ppb).¹

The significance of developing an efficient, large-scale remediation method for the removal of TCE-contaminated soils and groundwaters cannot be overstated. Common remediation technologies used to remove TCE from contaminated sites in the past, such as air stripping and soil venting, merely shift the VOC to another medium.⁴ Modern regulations, namely Section 121 of the Comprehensive Environmental Response, Compensation, and Liability Act, require off-gases to be treated before release into the atmosphere, negating the cost effectiveness of these traditional methods.⁴ Additional methods commonly used by scientists to degrade and mineralize TCE include advanced oxidation processes, the Fenton reaction, vacuum ultraviolet, and ultraviolet (UV) irradiation.¹ Advanced oxidation processes generate highly reactive hydroxyl radicals and have been increasingly accepted as promising methods for the degradation and mineralization of many organic pollutants.⁴ Photoactivated processes, such as the degradation of TCE with UV and titanium dioxide (TiO₂) as investigated in this study, are a class of advanced oxidation processes.¹ In recent decades, photochemical processes have become increasingly studied in the application of treating contaminated surface and groundwaters.⁵ These processes are characterized by the free radical mechanism initiated as the catalyst interacts with photons of a certain energy level, known as photocatalytic oxidation. When light of equal or greater energy than the bandgap energy ($\Delta E_{bg} = 3.1\text{-}3.4\text{ eV}$ for brookite TiO₂) illuminates the photocatalytic surface, electrons are excited from the valence band to the conduction band.^{5,6,7} This excitation results in a positive hole (h^+) in the valence band and an electron in the conduction band.⁸ The positive hole formed in the valence band oxidizes pollutants or water to produce hydroxyl radicals, as depicted in Figure 1. The electron excited to the conduction band reduces the oxygen adsorbed to the photocatalyst. The reduction of oxygen and oxidation of contaminants must occur simultaneously to promote efficient photocatalytic oxidation.⁵

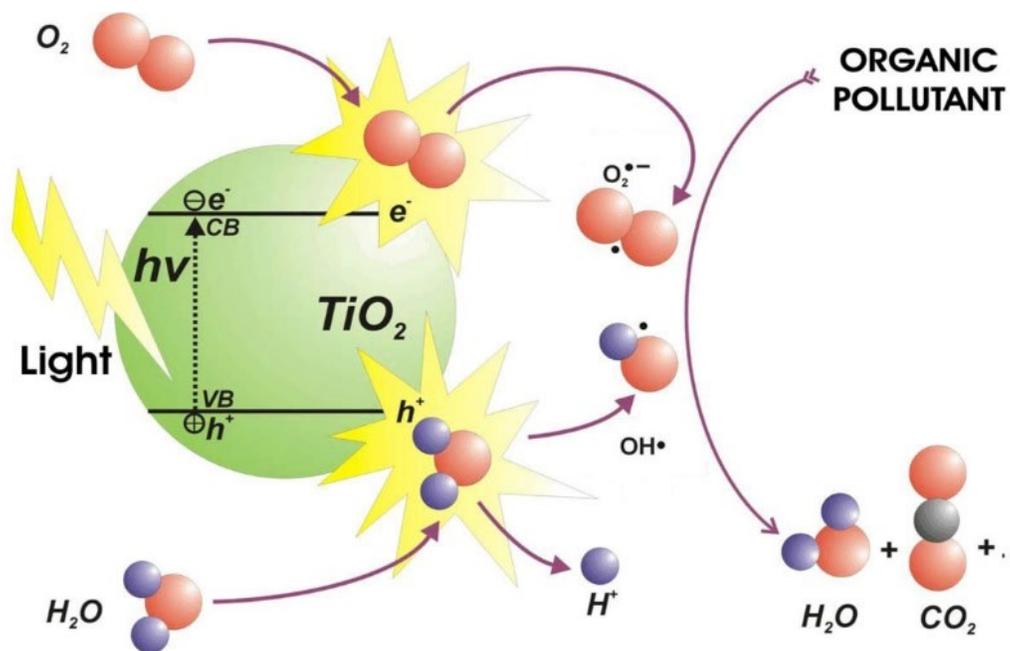


Figure 1. Reactions simultaneously occur as the TiO₂ surface is illuminated by UV light.⁹

Semiconductors such as TiO₂ are widely used in photocatalysis due to their favorable electronic structure, light absorption, charge transport characteristics, and excited-state lifetimes.⁵ TiO₂ nanoparticles (NPs) specifically are

extensively used in photocatalytic reactions due to their low cost, ease of handling, and resistance to decay from light.¹⁰ TiO₂ has varying photocatalytic ability that depends on band gap energy, phase structure, crystal size, specific surface area and pore structure.⁷ It is hypothesized the smaller the TiO₂ NP, the larger the surface-area-to-volume in solution, and the higher catalytic efficiency in removing pollutants.¹⁰ TiO₂ NPs exist in three main phases: anatase, rutile, and brookite, each morphology varying in structure, size, band-gap energy, and semi-conductor type.^{7,11,12} The structures of the three morphologies are compared in Figure 2.

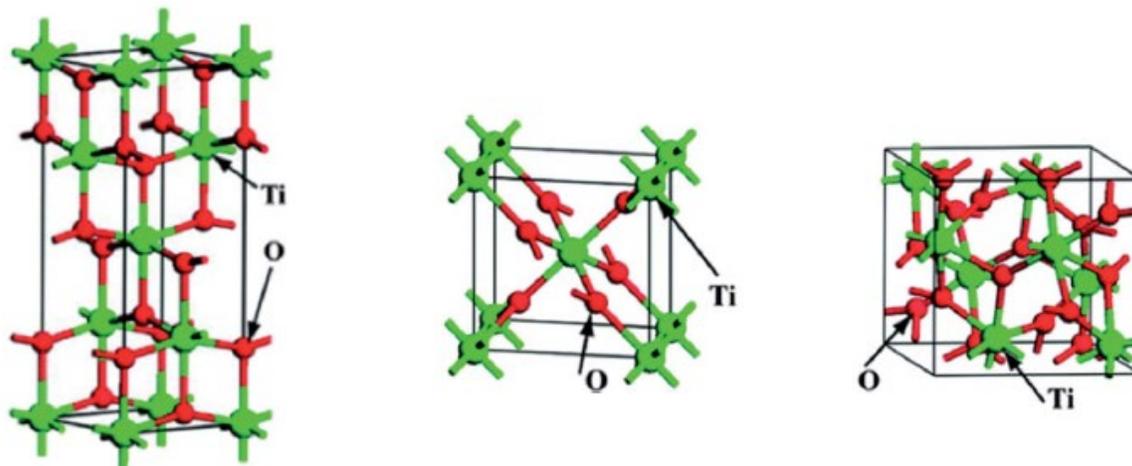


Figure 2. TiO₂ varies in morphology depending on synthesis conditions, and the three main polymorphs are anatase, brookite, and rutile (pictured left to right).⁷

The specific morphology of a photocatalyst influences its chemical properties.¹ Anatase is an indirect semi-conductor, while brookite acts as a direct semi-conductor like rutile.⁷ While rutile and especially anatase have been studied extensively in the application of photocatalysis, brookite has received less attention due to its complex structure, peculiar surface activity, and challenging synthesis.⁷ The average experimental band-gap energies of anatase and rutile have been established as 3.2 eV and 3.0 eV, respectively, while the band-gap energy of brookite has a wide range, between 3.1-3.4 eV.⁷ Brookite also displays a hybrid nature between rutile and anatase regarding density, stability, and refractive index.⁷ The crystalline structure and surface of brookite, in terms of exposed facets, acidic properties, and redox behavior is unique.⁷ In brookite, the Ti⁴⁺ type and abundance formed on exposed crystalline facets, and Ti³⁺ sites, formed by Ti⁴⁺ reduction can self-dope and withstand oxygen vacancies.⁷ TiO₂ NPs also exist in combinations of the three crystalline phases. For example, anatase-brookite is a TiO₂ polymorph found to outperform pure-phase brookite in the visible spectrum of light due to its relative band alignment.⁷ The absorption is shifted to the visible range, likely due to interparticle charge from the valence band of one phase to the conduction of the other.⁷ Additionally, TiO₂ crystal size is smaller in mixed phases than pure phases, as crystalline growth is limited when two phases form simultaneously.⁷

Until recent years, most attention to brookite reported its difficult synthesis, heavily documented since the 1950s, rather than its potential as an efficient photocatalyst due to its unique structure.⁸ Unlike the tetragonal structures of anatase and rutile, pure brookite has an orthorhombic crystalline structure composed of octahedra, each with a titanium atom at its center and oxygen atoms at its corners.⁸ The octahedra share edges and corners with one another and are distorted to present the oxygen atoms in two different positions. The formation of different TiO₂ polymorphs depends on how the TiO₆²⁻ octahedral units share edges and corners; brookite shares three, while anatase shares four and rutile shares two.⁷ This arrangement of the octahedra creates small tunnels along the c-axis of the crystalline structure, allowing penetration by small cations such as hydrogen. These tunnels are depicted in Figure 3. The open and not-so-dense brookite structure could help the stabilization of vacancies not only at the surface, but at the bulk of the material in photochemical and electrochemical processes.⁷

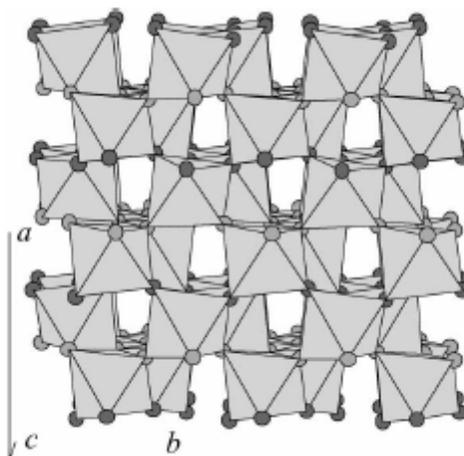


Figure 3. The arrangement of brookite octahedra creates small tunnels.⁸

2. Previous Studies

Previous research by Dr. Love's group focused on elucidating the unique properties of brookite differentiating it from other TiO₂ polymorphs. Nataliya Stynka and Shawn Overcash of Dr. Love's group studied how pH affects the form, shape, and size of brookite NPs during synthesis. Nataliya found that brookite was synthesized at pH 10.50 and 12.50. While rutile and anatase formation favored acidic pH conditions, brookite nanoparticles began to agglomerate as pH and heating temperature were increased.¹³

A relationship between pH and rate of the degradation of VOCs in the presence of brookite has not been established. The pH of solution affects many factors, such as the electrostatic interactions between the TiO₂ surface, solvent molecules, and substrate and charged radicals formed during the degradation of TCE.¹

Mehos and Turchi conducted a solar detoxification field experiment using Degussa P25 75% anatase/25% rutile TiO₂ and UV to remediate groundwater contaminated with TCE. Although the researchers tested four variables: pH, catalyst loading, flow velocity, and solar intensity, most were negligible aside from the pH effect.¹⁴ TCE degraded most quickly in deionized water, likely due to the absence of interference from other nonhazardous species in the water. The researchers hypothesized lowering the pH of the groundwater significantly improved the photocatalytic degradation of TCE by converting the hydroxyl-scavenging bicarbonate ions to CO₂ at pH 5.¹⁴

Though omitting UV and instead using under pressure dissolved oxygen, Hoseini et al. also found a significantly higher rate of TCE degradation with acidic pH in a study on the H₂O₂/TiO₂ advanced oxidative process with Degussa P25.¹⁵ The researchers found significant differences in TCE degradation rate at pH 4, pH 7, and pH 10, with pH 4 having the highest rate and pH 10 having the lowest rate. They stated that although the acidic conditions appeared to enhance catalysis by the anatase/rutile particles, the underlying mechanism is unknown.

Ndong et al. investigated the degradation of TCE and 1,1,1-trichloroethane, a similar chlorinated solvent, over UV irradiation alone and coupled with anatase TiO₂ nanosheets at pH 3, pH 7, and pH 11. While an inhibitive effect on degradation of 1,1,1-trichloroethane was observed in the acidic and basic solutions, the effects of pH on the degradation of TCE was negligible.¹ The degradation of TCE was effective in UV irradiation both alone and when coupled with TiO₂. Complete decomposition of TCE was observed at all pH levels tested.¹

The results from previous studies suggest that TiO₂ nanoparticles may be used for a wide range of pH to remove TCE from contaminated sources. While some groups reported the highest TCE degradation rates in acidic conditions, other groups found no significant difference at various pH. The purpose of this research is to similarly investigate the pH effect on the degradation of TCE with TiO₂ nanoparticles using UV irradiation. Instead of using commercial

anatase/rutile mixtures; however, this study implements less-commonly studied brookite to observe its photocatalytic efficiency over a wide range of pH.

3. Experimental Methods

3.1 Safety

Precautions were taken to limit exposure to TCE. Safety glasses and nitrile gloves were worn along with proper clothing and footwear to protect from spills. Care was taken to keep VOCs away from heat, sparks, and flame by storing in tightly closed containers and covering in Parafilm.

3.2 Materials

TCE stock (>99.5%) was purchased from Sigma-Aldrich. Brookite TiO₂ NPs (<100 nm) were also purchased from Sigma-Aldrich. The calibration mix was purchased from Fischer Scientific. Materials were stored in refrigerator when not in use and kept in a Styrofoam cooler during sample analysis. Exposure to light and air was limited to prevent the evaporation of VOCs. Concentrated NaOH and 6 M HNO₃ and were used to raise and lower pH, respectively.

3.3 Calibration Curve

EPA method 524.2 was followed to generate calibration curves for this experiment between 5-50 ppb. Ten microliters of 15 ppb internal standard and 5 ppb calibration were injected into a 5-mL syringe filled with deionized water and then into a Teledyne Tekmar Stratum Purge and Trap. Helium gas was used to extract the VOCs and samples were analyzed with a Shimadzu GCMS-QP2010 Plus Gas Spectrometer. A calibration curve was created by plotting TCE concentration on the x-axis, and the area of TCE divided by the area of 1,4-difluorobenzene on the y-axis. New calibration points were added to the curve each day of research.

3.3 Preparation of Samples

Purchased TCE was diluted to approximately 40 ppb to fit into the calibration curve. The pH of solution was adjusted using concentrated NaOH and 6 M HNO₃ and measured using a Vernier pH probe with Logger Lite version 1.9.4 software.

The resulting solution was divided into 40-mL amber glass vials, some containing 2.0 mg brookite. The vials were covered in Parafilm and aluminum foil, sonicated for five minutes, and stored in the refrigerator until analysis to prevent loss of volatile organic compound analytes.

3.4 Photodegradation Experiment

Samples were sonicated for 5 minutes before 5-mL were collected into a syringe that was clipped directly into the Rayonet Photochemical Reactor. The samples were exposed to irradiation for 30, 60, and 90 second intervals at 254 nm wavelength.

3.5 Sample Analysis

The samples were injected into a Teledyne Tekmar Stratum Purge and Trap using helium gas and analyzed with a Shimadzu GCMS-QP2010 Plus Gas Spectrometer.

4. Results and Discussion

4.1 Calibration Curve

The calibration curve yielded the equation $y = 0.014x - 0.0027$ with an R^2 value of 0.983 and is shown in Figure 4. The Limit of Detection was calculated to be 6.16 ppb. The Limit of Quantitation (LOQ) was found to be 18.66 ppb. The values obtained from least squares regression can be found in Table 1.

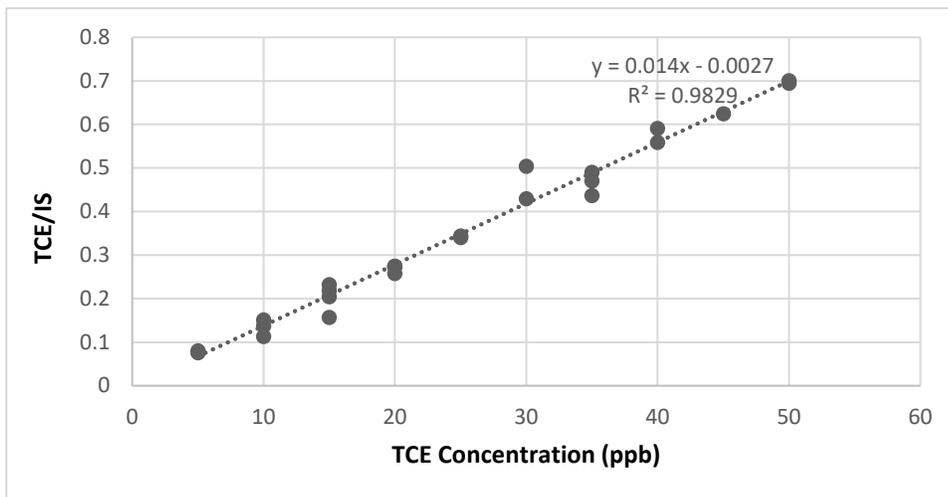


Figure 4. A calibration curve was established to determine relative concentrations of TCE.

While the LOQ is too high to quantify TCE concentrations as low as the EPA limit of 5 ppb, the equation obtained from the least squares regression was used to provide calculated estimates for the TCE concentrations by using the integrated areas for TCE and 1,4-difluorobenzene obtained from Gas Chromatography Mass Spectrometry (GC-MS) analysis in the same time frame.

Table 1. Values obtained from the least squares regression for the calibration curve

Slope	Uncertainty of Slope	y-intercept	Uncertainty of y-intercept	R^2	S_y	F statistic	df	Regression Sum of Squares	Residual Sum of Squares
1.40×10^{-2}	3.80×10^{-4}	-2.73×10^{-3}	1.04×10^{-2}	0.983	2.62×10^{-2}	1378	24	0.947	0.0165

4.2 pH studies

Experiments were performed at pH 1.3 and pH 12 with brookite and without brookite at 254 nm UV irradiation. The effect of reducing the pH on the photodegradation of TCE was investigated and the data collected was plotted in Figure 5.

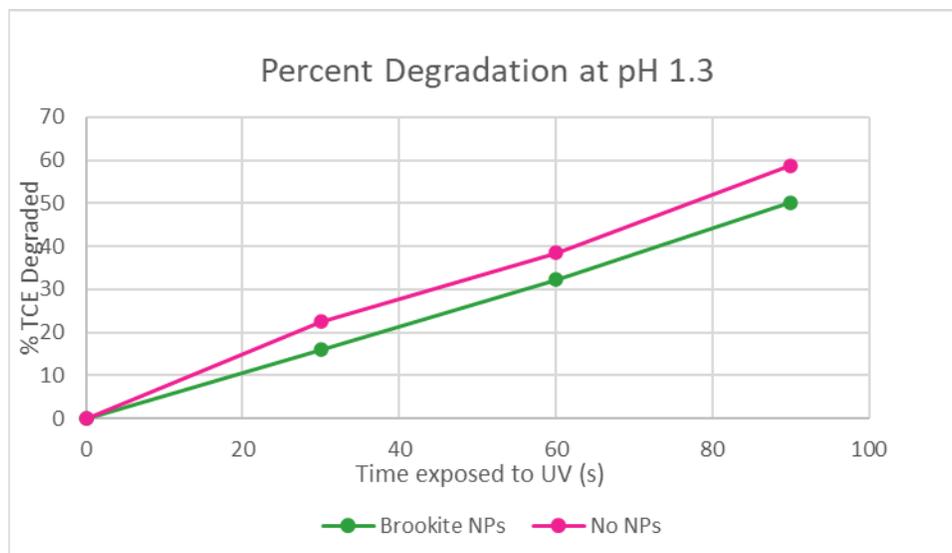


Figure 5. Samples without brookite outperformed those with brookite in degrading TCE in highly acidic solutions.

Although the samples without brookite were found to have a slightly higher rate of degradation of TCE than samples with brookite at pH 1.3, the results are overall very similar. After 30 seconds of UV, the sample containing brookite had only degraded 16.0%, while the sample without brookite had degraded by 22.5%. After 60 seconds, the brookite sample showed a degradation rate of 32.3%, while the sample without the addition of a photocatalyst displayed a degradation rate of 38.5%. After 90 seconds, the brookite sample degraded TCE by 50.1%, while the sample without brookite degraded TCE by 58.8%. All samples displayed a rather linear decrease in TCE concentration during this time interval as time exposed to UV increased, a phenomenon supported by previous studies. While it is interesting that the samples without brookite experienced a higher percent degradation than those with brookite, additional experiments are necessary to determine the reproducibility of these findings.

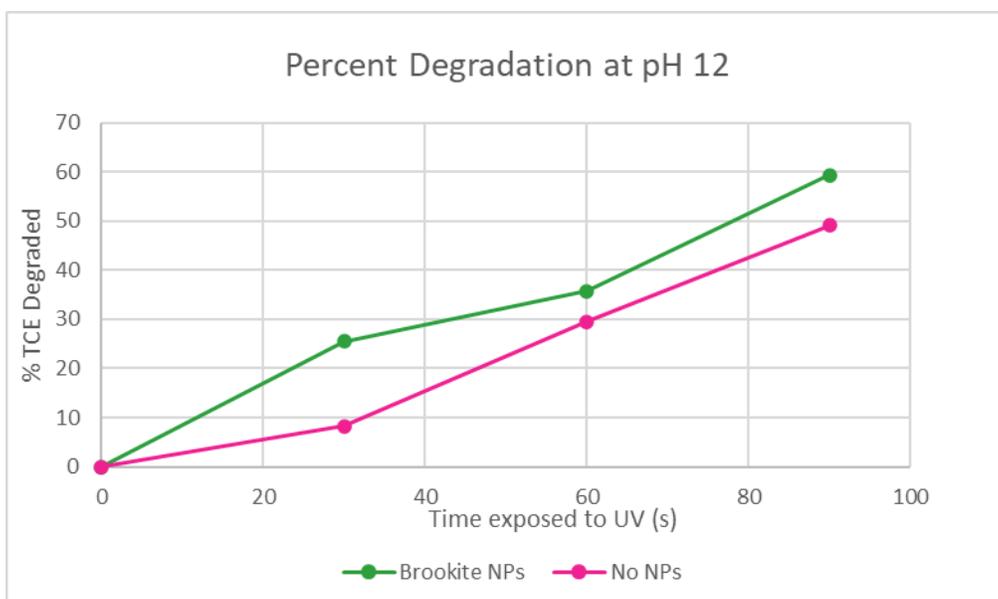


Figure 6. Brookite samples degraded TCE at a higher rate than samples without brookite at pH 12.

The data collected from the basic pH trials is plotted above in Figure 6. The experiments conducted at pH 12 also agreed with previous studies by demonstrating a decrease in TCE concentration as the time exposed to UV irradiation increased, both with and without the addition of brookite. Unlike the samples from the acidic pH study, the basic pH study showed an improvement in the rate of degradation in samples containing brookite over those without brookite. After 30 seconds, the pH 12 brookite sample was found to have degraded 25.4%, while the pH 12 sample without particles displayed a degradation rate of 8.2%. After 60 seconds, the basic sample containing brookite had degraded TCE by 35.7%, while the basic sample without brookite had only degraded by 29.5%. After 90 seconds, the brookite sample degraded TCE by 59.4%, while the sample without NPs had only degraded TCE by 49.1%. While it is evident that the samples containing brookite showed a higher rate of degradation of TCE at basic pH than those without, additional studies are needed to determine reproducibility.

5. Conclusion

The preliminary studies implementing pH manipulation agreed with the literature in that as time exposed to UV irradiation increased, the concentration of TCE decreased. This trend is apparent in both acidic and basic solutions containing brookite, as well as in acidic and basic solutions without the addition of brookite as a photocatalyst. While researchers Mehos and Turchi, as well as Hoseini et al., claim that acidic pH favors the highest rate of degradation with commercial Degussa P25 75% anatase/25% rutile, this relationship was not observed with brookite particles in this study.^{14, 15} Experiments conducted with brookite at acidic pH in this study demonstrated a lower rate of degradation than those conducted with brookite at basic pH. These results suggest implementing brookite as a photocatalyst would increase the rate of degradation of TCE. In very acidic conditions, however, a higher rate of degradation of TCE may be observed without the presence of brookite in solution.

Future experiments are necessary to probe the rate of degradation at unadjusted pH to compare to the experiments performed at pH 1.3 and pH 12 with brookite. Implementing longer durations of UV irradiation would lead to a better understanding of the photocatalytic efficiency of brookite. Although the LOD from the calibration curve is higher than the EPA limit of 5 ppb, future studies should investigate how many seconds of UV exposure result in a TCE concentration around this value. An additional study on kinetics would be useful to define the order of reaction of TCE degradation with brookite, as well as implementing additional photodegradation trials to determine brookite's overall efficiency as a photocatalyst in degrading TCE.

6. References

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