Comparative Analysis of Titanium Dioxide Nanoparticles in Anatase vs. Rutile Crystal Phases for the Purpose of Water Treatment

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Abstract

Gas Chromatography Mass Spectrometry (GC-MS) was used to analyze aqueous samples of known trichloroethylene (TCE) concentrations before and after treatment with titanium dioxide nanoparticles (TiO_2 NPs). TiO_2 NPs were pressed into pellets and heated to 600°C for 2 hours in a furnace before being placed into glass vials containing aqueous TCE solution. The zero-headspace vials were refrigerated until analysis. Additionally, TiO_2 pellets were assessed with X-ray powder diffraction yielding the result that 30 nm diameter anatase phase particles underwent full transition to rutile phase. The results show that samples treated with TiO_2 NPs of anatase or rutile crystal phase were not found to have mean TCE concentrations different than that of controls, and therefore it can be concluded that TiO_2 NPs neither reacted with nor degraded TCE.

Nanoparticles, Trichloroethylene

1. Introduction

Human and animal life is dependent on adequate amounts of potable water. While biological contaminants such as microorganisms are often the focus of water filtration efforts, other contaminants such as pesticides, pharmaceuticals, and cleaning products are also of growing concern. Dubbed "emerging contaminants" (EC's), these organic compounds have likely been entering surface and groundwater since humans began using them.[1] One of the most notable concerns regarding the pervasive presence of these contaminants is the exhibition of endocrine disrupting effects on humans and wildlife, especially from pharmaceutical residue and steroid hormones.[1,2,3] Even when concentrations are low (ppb), the persistent exposure to EC's is cause for concern due to potential bioaccumulation and synergetic toxicity.[4] Water purification is an issue faced by both undeveloped and developed countries. In developed countries where it has become customary to rely on wastewater treatment facilities to provide water that is free of biological contaminants, drug residues and chemicals are still found in drinking water, groundwater, and wastewater treatment effluents.[1] While reverse osmosis filtration membranes effectively remove organic, inorganic and biological compounds, the concentrated contaminants pose a problem when it is time to safely clean or dispose of the membrane and the amount of energy input for cleaning is large.[5] Therefore, the present research focuses on utilization of titanium dioxide nanoparticles (TiO_2 NPs) formed into a pellets as an alternative means to remove organic molecules in water. TiO_2 in the nanoparticle form holds particularly novel and exploitable properties due to the large surface area-to-volume ratio.[6,7] Metal oxides are known to have sorption properties for polar organics due to the presence of surface defects, such as absent oxygen atoms within the crystal matrix.[8,9] Due to more surface defects (oxygen vacancies) per volume for nanocrystals vs. microcrystals, nanocrystals exhibit higher reactivity.[8] The research of Guo et al., suggests that surface hydroxyl groups also play a role in TiO_2 reactivity towards organics.[10]

A contaminant of specific concern is the organic molecule trichloroethylene (TCE). TCE is a widely used industrial solvent, utilized primarily for cleaning and degreasing metal prior to electroplating or other industrial processing.

TCE has been identified as a widespread contaminant and is classified as a human carcinogen by the International Agency for Research on Cancer and the United States Environmental Protection Agency. Human TCE exposure via oral and inhalation routes is of concern primarily due to the metabolism of TCE into numerous unstable and reactive intermediates within the body, including TCE epoxide, chloral hydrate, and trichloroacetic acid.[11,12] The instability of these metabolites leads to the likelihood of adduction reactions with biological targets.[11] Once TCE has entered soil and therefore groundwater, it is difficult to contain or remove, and hence has the potential to rapidly contaminate any water emanating from that area. The EPA limit for safe drinking water requires that TCE concentration be below 5 ppb. Current methods, such as sparging, for remediating TCE-contaminated sites are expensive and often only provide limited removal or degradation of the compound. Therefore, research focused on alternative techniques is of significance.

Based on evidence of reaction of TiO_2 and TCE in photocatalytic applications, TiO_2 NPs are here examined for potential to react with and remove contaminants from water. While the mechanism of binding has yet to be elucidated, evidence of interaction between TiO_2 and TCE exists.[13] The research of Ndong et al. suggests that the generation of radical oxygen species lead to the dechlorination of aqueous phase TCE in UV/TiO_2 systems.[13] The current investigation focuses on particle size and crystal phase of the TiO_2 NPs, and the role these variables play in fostering reaction with aqueous TCE *in the absence of UV light*. Rutile and anatase are the most common phases of TiO_2 NPs, with rutile being the lower energy conformation. According to Ndong and Bakardjieva et al., anatase is the more reactive phase for photocatalytic applications.[13, 14] The current research aims to identify if the concentration of TCE in water samples decreases upon treatment with a TiO_2 NPs pellet, with analysis performed via GC-MS. In addition, X-Ray Powder Diffraction was used to probe the relationship between temperature, nanoparticle diameter size, and the phase shift from anatase to rutile crystal structure.

2. Experimental Methods

TiO_2 NPs were purchased from Sigma Aldrich and pressed into pellets using the Parr pellet press. All pellets contained ~ 0.5 g of TiO_2 NPs. All pellets were heated in lidded ceramic crucibles inside a furnace at 600°C for 2 hours. Trials were conducted with pellets being heated to 200°, 400°, and 500°C, but all of these samples exhibited significant shattering and dispersion upon contact with aqueous solution. Therefore, all further trials were conducted using the 600°C pellets as these remained intact in solution. Pellets were then characterized before and after heating with Philips X'Pert X-Ray Powder Diffractometer using CuKα radiation to establish average crystallite (particle) size.

TCE was obtained from Sigma Aldrich and Hamilton brand gastight syringes were used to prepare an aqueous solution. All glassware and 20 mL Teflon capped vials used in this process were rinsed in triplicate with ultrapure water and then baked in a VWR Symphony oven at 105° C for 1 hour. One pellet of known mass was placed in each of the 20 mL vials and the TCE solution was added until a meniscus formed at the top, then the vial was sealed, inverted to check for absence of bubbles, and placed in a refrigerator until sample analysis. The final set of samples was treated with 1.0 grams uncompressed 5 nm powder in each vial rather than a pellet. Samples were analyzed using a Shimadzu model Gas Chromatograph Mass Spectrometer GC-MS-QP2010 plus with a Teledyne Tekmar Stratum Purge and Trap. A total of 5mL of each sample was drawn into a gastight syringe with 10 µL of the 15 ppm internal standards (IS), bubbled helium through it in the purge and trap inlet, and then injected. A calibration curve was created with volatile organic compound solution of known concentrations (Figure 1). Due to the peak area instrument response for TCE divided by the peak area instrument response of the internal standard bearing a direct relationship to concentration, solutions of unknown concentration can be quantified with this method.
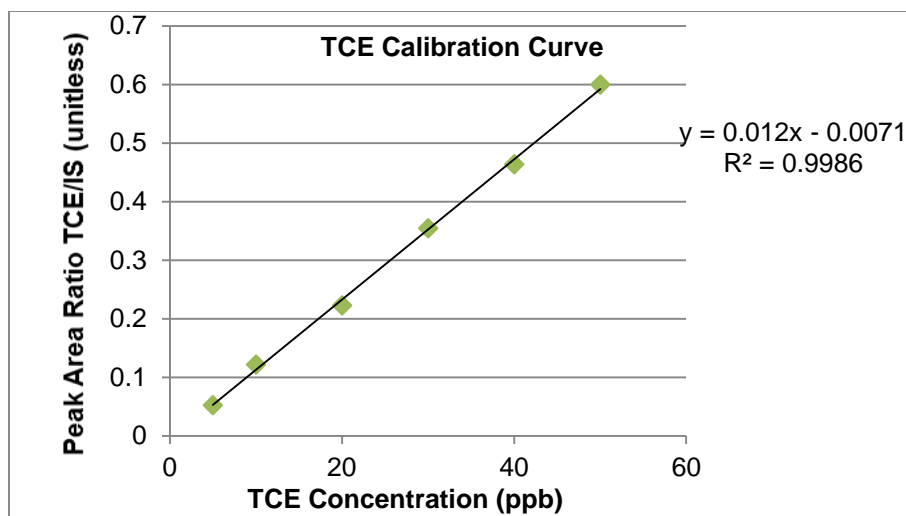
Figure 1. Calibration Curve for TCE Standard Solutions.

3. Results and Discussion

3.1 X-Ray Powder Diffraction results

Anatase and rutile 21 nm and 30 nm TiO_2 NPs were heated to 500°C and 600°C in the furnace. X-ray powder diffraction (XRD) analysis was performed on untreated NPs before and after heating (Table 1). 21 nm Anatase NPs resisted a phase change when heated to 500°C or 600°C as evidenced by the retention of a peak at 25.3 °2θ (Figure 2) and small average NPs size change (Table 1). 30 nm anatase TiO_2 NPs were influenced by heating, as suggested by the development of a peak at 44.6 °2θ (Figure 3). This peak is associated with the (210) face of rutile, indicating that a shift to rutile phase corresponds with the increase in particle size (Table 1).

Bakardjieva et al.'s results showed that a complete transition from anatase to rutile did not occur until 800°C and that at 600°C their sample was composed of 39.6% anatase and 60.4% rutile. At 700°C, their sample consisted of 1.5% anatase and 98.5% rutile. In contrast, our data show that 30 nm anatase TiO_2 NPs underwent a complete transition to rutile at 600°C for 2 hours, while 21nm diameter particles resisted this shift. (Table 1.) Bakardjieva et al. reported that larger anatase crystals transform more readily than smaller particles, and that product rutile occurs in a coarsened form in comparison to the reactant anatase. This provides a possible explanation for why the 21nm particles resisted the transition whereas the 30 nm particles did not.

Based on the current findings, it would be expected that anatase and rutile pellets would behave similarly in their response to aqueous TCE, as these pellets are actually both in the rutile crystal phase after heating. The GC-MS data support this, as when the mean concentrations of samples treated with anatase vs. rutile pellets were compared at a 95% confidence interval using the Student's t-test, the means were found to be not statistically different.[15]

Table 1. Average size of TiO$_2$ NPs determined by XRD analysis.

Sample Name	Peak Position [°2θ]	Average Crystallite Size [Å]	Average Crystallite Size [nm]
21nm AnataseTiO2 Untreated	25.28	270	27
21nm Anatase TiO2 @ 500°C/2 hr.	25.367	257	26
21nm AnataseTiO2 @600°C/2hr.	25.327	292	29
30 nm Anatase Untreated	25.37	239	24
30 nm Anatase @600°C/2hr.	44.62	1073	107
30 nm Rutile Untreated	27.531	222	22
30 nm Rutile @600°C/2hr.	44.61	94	90
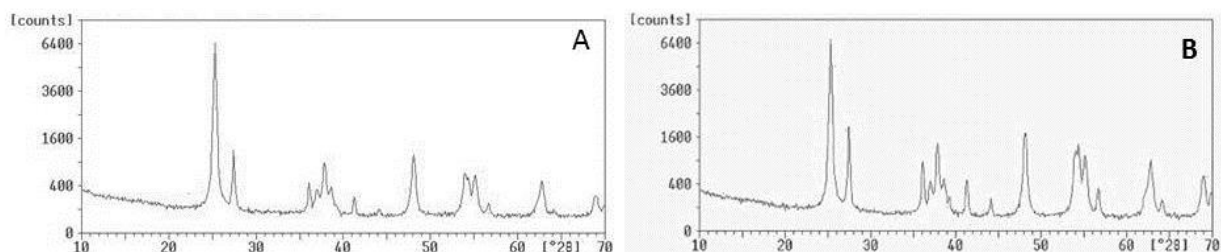
Figure 2. 21 nm Anatase Peaks before (A) and after (B) heating to 600°C for 2 hours.
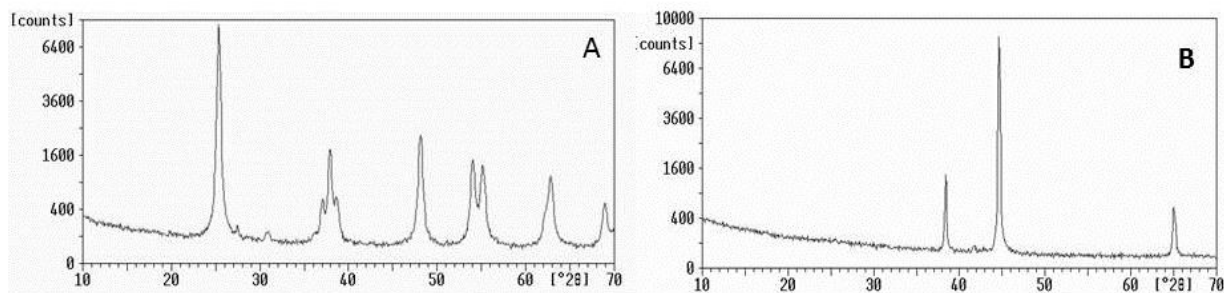

Figure 3. 30 nm Anatase Peaks before (A) and after (B) heating to 600°C for 2 hours.

3.2 GC/MS Results

The data presented in Figure 4 depicts the results of all sets of trials with TCE concentrations pre- and post-treatment with TiO$_2$ NPs. TiO$_2$ NPs were not found to reduce TCE concentration in water when the mean values from treated samples were compared with the concentration values from corresponding control (untreated) samples. The 21 nm anatase, 30 nm anatase, 30 nm rutile pellets, nor the 5 nm anatase NPs yielded post-treatment TCE concentrations that were statistically different from untreated solutions, nor were they statistically different from replicate trials of the same type of pellet. Experimental result concentrations were pooled and the mean value and concentration of the control (reference value) for each set of trials was used to calculate the Student's t-value. Experimental t-value was compared to the critical t-value at the 95% confidence interval, and was found to be less, leading to the conclusion that the TCE concentrations were not statistically different.[15]
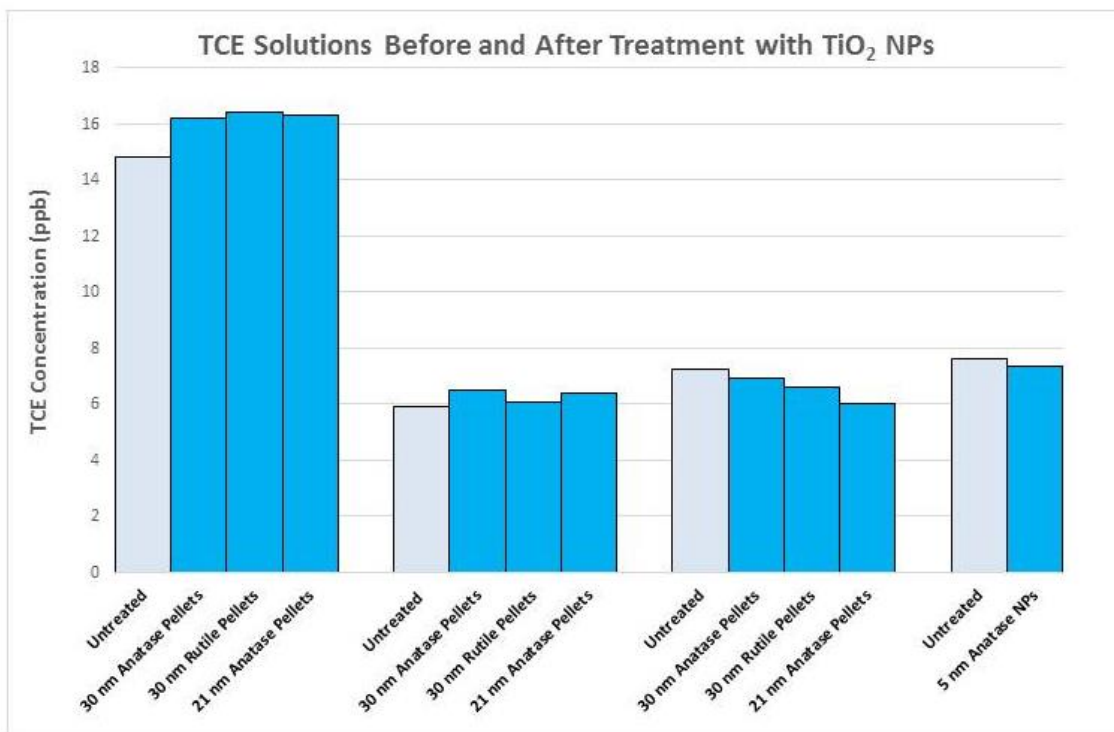
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Figure 4. TCE solutions before and after treatment with 30nm and 21nm anatase and rutile TiO$_2$ NPs based pellets, and 5nm anatase TiO$_2$ NPs.

Each cluster shows a different set of trials, with the light blue bar depicting an aqueous solution of TCE and the associated darker blue bars showing the concentration post-treatment. While the starting concentration of TCE varied per set, none of the trials yielded statistically significant reduction of TCE concentration regardless of the size or type of TiO$_2$ NP's with which it was treated.

4. Conclusion

4.1 Reactivity of TiO$_2$ towards Trichloroethylene

The present investigation did not find TiO$_2$ NPs of either anatase or rutile crystal structure to be effective at reacting with TCE in aqueous solution. Based on the findings of Ndong et al. in comparison to the present research, it appears that UV light is essential for promoting reaction between TiO$_2$ and trichloroethylene for the purpose of water purification.[13] Future research will focus on aqueous solutions of organic molecules with functional groups other than the single carbon-carbon double bond characteristic of TCE in regards to their reactivity towards TiO$_2$ NP's .

4.2 Crystal phase shift results

 Anatase NP's of 30 nm diameter size heated to 600°C have undergone a phase shift to rutile. The XRD spectra (Figure 3) of the smaller 21nm diameter particles heated to the same temperature appear similar before and after heat treatment. Anatase undergoes an irreversible phase change to rutile when heated to a temperature between 400-1200°C, but lacks one specific temperature where this occurs because pressure, sample size, grain size, and presence or lack of O$_2$ affect

the material's ability to make this shift.[16] The research of Riyas et al. suggests that rutile grain growth is associated with an increase in crystallite size,[17] and these results are supported by the current research (Table 1.) However, the current investigation's results were in contrast to the work of Ding and Li, as these researchers found anatase of larger grain size transitions more slowly to rutile than that of smaller grain size.[18]

5. Acknowledgements

6. References

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