Characterization of Titanium Dioxide Nanoparticles via X-Ray Diffraction and Scanning Electron Microscope

Abstract

The presence of contaminants such as pesticides and pharmaceuticals in drinking water is of great concern because these compounds are still present even after the water has been filtered to remove microorganisms. This investigation focuses on the use of titanium dioxide nanoparticles (TiO_2 NP's) as a water filtration medium. The large surface area-to-volume ratio of NPs make them capable of interaction with functional groups of organic molecules, therefore binding the organic molecule to the surface of TiO_2 NPs. X-ray diffraction and Scanning Electron Microscope will be used to characterize nanoparticles before and after reaction with aqueous solutions of contaminants. Calcination at varying temperatures will be employed to form durable pellets that can be used for investigating potential reaction with organics. Aqueous solutions will be assessed with UV-Vis before and after exposure to the pellets to determine the effect of TiO_2 NP's on contaminant concentration.

Background

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 NP's) formed into a pellet 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] Ultimately, the goal of our research is to develop a pellet that will bind fully with the organic contaminants in water. After reaction, the pellet can be removed from the water with the contaminants bound to it, therefore effectively reducing the concentration of those contaminants in the water. Additionally, it is important that the pellet itself remain solid during reaction, so as to avoid introducing any TiO_2 into the water sample.

X-ray diffraction is a common analytical technique for characterization of TiO_2 NP's.[10,11] X-ray diffraction is an analytical technique in which monochromatic radiation is directed at a sample, and constructive interference along with a diffracted ray is produced upon interaction between the sample and the X-ray. The conditions must satisfy Bragg's Law which states that $n\lambda=2d\sin\theta$. The law forms a relationship between the wavelength of the electromagnetic radiation and the diffraction angle and lattice spacing of a crystalline sample. The sample is scanned through a range of 2θ angles, and the resultant diffracted X-rays are then detected and counted. Converting the diffraction peaks to d-spacings utilizing Bragg's equation allows the mineral to be identified because each mineral has a unique set of d-spacings.[12] The size and crystal structure of TiO_2 NP's impacts their ability to react with organic molecules. Collecting images with the SEM, ideally at 200nm resolution, will provide visual information regarding the arrangement of nanoparticles at the surface of the pellet. Understanding the composition of the TiO_2 NP's at the molecular level will aid in understanding what functional groups will be able to react with the NP's, and how the NP's may need to be modified in order to further encourage reactivity.

Methods

The X-ray diffractometer (XRD) and Scanning Electron Microscope (SEM) will be used to collect data from purchased and synthesized titanium dioxide nanoparticles for the purpose of crystal structure characterization before and after reaction with organic molecules such as the pesticide atrazine. Experience will be gained in sample preparation techniques and utilizing Bragg's Law equation to interpret the collected data. The results will be examined with respect to the current literature, with a focus on identifying binding between organic molecules and the TiO_2 NP's. In the first step of research, the TiO_2 NP's will be characterized in an unreacted state. In the second step, the TiO_2 NP's will be exposed to aqueous solutions of common organic contaminants, then characterized again via X-ray diffraction to establish whether changes to their crystal structure occur upon exposure to, and possible binding with, organic molecules. Having a clear understanding of the reaction occurring at the molecular and atomic level is of key significance to the overall research project. The SEM will be used to examine the topography of the surface of the pellet as well as the interior, and the XRD will be used to quantify particle size. Additionally, a continuation of last summer's research goal of forming NP's into a more solid pellet that can withstand submersion in water will be pursued based on new information regarding calcining pellets in the oven and then dipping them in TiO_2 sol-gel.[13]

Conclusion

The results of this research will serve to inform the goals of the overall research project, which is to develop effective water filtration technology based on TiO_2 nanoparticle filters. Understanding how organic molecules bind to the surface of the nanoparticles is key to developing functional filters, as well as understanding modifications that may need to be made to target specific organics such as pesticides and pharmaceuticals. Trials with newly developed TiO_2 pellets will involve quantifying the amount of atrazine or other chemicals removed from the water via UV-Vis.

References

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Budget and Justification

Student stipend for 8 full-time weeks of summer research

$ 1500.00

Materials for Research

1. Titanium Oxide (TiO_2) Nanoparticles / Nanopowder (TiO_2 Anatase, 99.5%, 5nm)
   US Research Nanomaterials, Inc. **Stock #:** US3838
   $129/100g
   http://www.us-nano.com/inc/sdetail/20769

2. Titanium Oxide (TiO_2) Nanoparticles / Nanopowder (TiO_2 Anatase, High Purity, 99.98%, 30nm) US Research Nanomaterials, Inc. **Stock #:** US3498
$135/100g
http://www.us-nano.com/inc/sdetail/7709

3. Titanium Oxide (TiO_2) Nanoparticles / Nanopowder (TiO_2 Anatase, High Purity, 99.5%, 15nm) US Research Nanomaterials, Inc. **Stock #:** US3492
$89/100g
http://www.us-nano.com/inc/sdetail/13037

4. Titanium Oxide (TiO_2) Nanoparticles / Nanopowder (TiO_2 Rutile, High Purity, 99.9%, 30nm) US Research Nanomaterials, Inc. **Stock #:** US3520
$79/50g
http://www.us-nano.com/inc/sdetail/276

5. Titanium Oxide (TiO_2) Nanoparticles / Nanopowder (TiO_2 Rutile, High Purity, 99.9%, 50nm) US Research Nanomaterials, Inc. **Stock #:** US3530
$79/50g
http://www.us-nano.com/inc/sdetail/7710

Having Titanium Oxide (TiO_2) Nanoparticles in 5nm, 15nm, and 30nm sizes will allow for comparisons as to the optimal size for reactivity. Having both Rutile and Anatase crystal forms will enable us to determine if one crystal structure is better suited to this particular application, or if the two forms have similar reactivity.

Materials Total	$511.00
Materials + Student Stipend	$2,011.00

Time Period

May 5, 2015-May 29, 2015 Characterization of nanoparticles and pellets with XRD and SEM
June 1, 2015- June 26, 2015 Formation of pellets and tests with aqueous solutions of contaminants

Publication Outlet

The results from this research will be submitted to the *UNC-Asheville Journal*. Additionally, a poster summarizing the research results and methodology will be prepared and presented at the UNCA Undergraduate Research Symposium