

**TiO₂-PHOTOCATALYZED ARSENIC(III)
OXIDATION AND ITS APPLICABILITY
TO WATER TREATMENT**

Thesis by

Megan Alameda Ferguson

In Partial Fulfillment of the Requirements for the

Degree of

Doctor of Philosophy

CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California

2006

(Defended January 31, 2006)

© 2006

Megan Alameda Ferguson

All Rights Reserved

ACKNOWLEDGEMENTS

First, I would like to thank my advisor, Janet Hering, for her support and advice throughout my time here. She has taught me how to structure my ideas, research, and writing more clearly, and by her example I have learned to critically assess scientific work. Mike Hoffmann's suggestions, encouragement, and knowledge have been critical to my understanding of TiO₂ photochemistry. George Rossman and Nate Lewis have both helped to broaden my research perspective.

Andrew Miller, my geography mentor at UMBC, has been instrumental in encouraging me to pursue opportunities that would benefit my research career and personal development. Discussions with AJ Colussi have contributed much to this research. Nathan Dalleska taught me the ins and outs of the ICP-MS and the LC systems and provided friendly advice (and countless waste disposal containers!) during my flow-through experiments. I would also like to thank Mike Vondrus for making my reaction cell, Diego Fernandez for help with running the high resolution ICP-MS, Lisa Cowan for training me in the collection and interpretation of XRD data, Carol Garland for assistance with immobilizing and grinding down my TiO₂-coated beads, Chi Ma for help with SEM, Angelo DiBilio for introducing me to EPR, and Chris Boxe for providing me with the materials and procedures for actinometry. Thanks also to Asahi Okada, whose SURF research constitutes a part of this work. The EPA STAR and NSF Graduate Fellowship Programs provided financial support for this research.

I appreciate the support and friendship of all the past and present members of the Hering and Hoffmann groups, particularly Rich Wildman, Azra Bilgin, Diana Stefanescu, Tao Cheng, Giehyeon Lee, Suvasis Dixit, Dan Giammar, Jennnie Stephens, Tim Lesko, and Marcelo Guzman. Special thanks to Kate Campbell, who has always had a sympathetic ear and good advice whenever things are going particularly well or poorly. The friendliness of Linda, Fran, Cecilia, Belinda, and Elena has made Keck a great place to work.

Lisa Welp and Rebecca Washenfelder have been fast friends throughout the ups and downs of research as well as for bike rides, camping, vegetable division, and many fine lunches. Jamie Lindfors and Dan Lieberman exposed me to the joys of pole vaulting, climbing, canyoneering, and generally living it up with outdoor activities. Mike Fleming is a fabulous ceroc partner and an even better friend. The ballroom dance crowd has often kept me awake long past my bedtime, but I always have a fantastic time and it is a great stress outlet. Kimball Martin has been a dear friend and roommate since college and is always there for me.

I thank my parents, Lyn and Tom Olson, for instilling in me a love of science, learning, and the natural world, and for their immeasurable love and support throughout my studies. Despite the distance, my sister Meryl's cell phone is always on if I need to laugh or vent. Finally, Alex has been the kindest, funniest, most thoughtful, and most supportive husband I could wish for. His company has truly made this journey a pleasant one.

ABSTRACT

Ingestion of arsenic (As) in drinking water can lead to several chronic illnesses, including bladder, lung, and skin cancers. Due to natural weathering reactions, As is present in many drinking water sources throughout the United States and other countries. The U.S. drinking water standard has recently been revised from $50 \mu\text{g L}^{-1}$ to $10 \mu\text{g L}^{-1}$, thus requiring thousands of water distribution facilities to implement new As removal procedures. However, most As removal technologies treat As(V) much more effectively than As(III), so a pre-oxidation step is recommended for source waters containing As(III) at significant concentrations. The photocatalyzed oxidation of As(III) on titanium dioxide (TiO_2) has been critically evaluated as a potential technology to achieve pre-oxidation.

Batch slurry studies showed that sorption of both As(III) and As(V) to TiO_2 occurs rapidly. Changes in As(III) concentration adsorbed to the TiO_2 surface, whether resulting from varying dissolved As(III) concentration or from the presence of competitive adsorbates, affected the rate of photooxidation. A transition from first-order to zero-order reaction kinetics was observed as the TiO_2 surface became saturated with As(III). Experiments targeting the reaction mechanism (which used hydroxyl radical quenchers, an alternate electron acceptor, and superoxide dismutase) suggested that superoxide plays a major role as an oxidizing agent in this system.

As(III) was rapidly photooxidized in a fixed-bed, flow-through reactor. Catalyst poisoning or severe mass transport limitations were not observed for the conditions studied, although complete As(III) oxidation could not be achieved due to constraints of

reactor geometry. With synthetic groundwater solutions, the reaction appeared to be inhibited by the presence of competitive adsorbates. Use of natural sunlight resulted in more rapid As(III) oxidation than that observed with irradiation from the 365 nm lamp used for other experiments.

As arsenic detection methods improve, reporting levels and perhaps regulatory standards will be lowered, requiring more distribution systems to consider technologies for As treatment. In contrast to methods of pre-oxidation currently in use, TiO₂ photocatalysis involves no hazardous chemicals and generates no toxic reaction byproducts. Based on these findings, TiO₂-photocatalyzed As(III) oxidation could be a viable pre-oxidation technology for certain small water distribution facilities.