Chapter 7

CONCLUSIONS

7.1 Summary of Results

TiO_2 irradiated with UV light has been shown to photocatalyze the oxidation of As(III) to As(V) under a variety of conditions relevant to water treatment. Batch slurry studies were used to explore the role of As sorption to TiO_2 and to elucidate the mechanism of oxidation. Fixed-bed, flow-through studies were conducted to determine how the system behaved under conditions more characteristic of water treatment and to evaluate the likelihood of catalyst poisoning. High resolution ICP-MS and other analytical techniques were considered for their potential to lower the practical quantitation limit for As, which could possibly lead to a lower MCL and cause more water distribution facilities to require As treatment. Based on these findings, pre-oxidation of As(III)-containing source waters using TiO_2 photocatalysis may be an efficient, cost-effective choice for certain small water distribution systems.

7.1.1 As(III) sorption and oxidation at the TiO_2 surface

The extent of As(III) photooxidation is dependent on As(III) sorption to the TiO_2 surface. Sorption equilibrium is achieved fairly rapidly, with significant sorption taking place within seconds and greater than 95% of total sorption occurring in less than 30 min. Isotherm studies conducted at pH 6.3 exhibited a sorption maximum of 32 $\mu M\ g^{-1}$ for As(III), whereas As(V) did not achieve a sorption maximum even at 127 $\mu M\ g^{-1}$. At the beginning and end of photooxidation experiments, when all As was present as As(III) (beginning) or As(V) (end), the distribution of dissolved and adsorbed As corresponded to that predicted by sorption isotherms. This suggests that sorption pseudo equilibrium was maintained. Increases in initial As(III) concentration caused a transition from pseudo first-order to pseudo zero-order reaction kinetics as the corresponding position on the sorption isotherm shifted from the linear region to the plateau region.

Experiments suggested that superoxide is a major oxidizing species in this reaction. Use of the alternative electron acceptor CCl_4 in the absence of O_2 severely inhibited the reaction (96% reduction in reaction rate constant), as did the addition of superoxide dismutase to aerated suspensions (73% reduction in rate constant). The hydroxyl radical quencher *tert*-butanol had no effect on As(III) photooxidation after sorption effects were accounted for; however, 2-propanol did slow the reaction by 33% while only slightly affecting sorption. Subsequent studies by other groups suggest that the valence band hole is also a major oxidant for As(III) on TiO_2.

7.1.2 Flow-through studies

As(III) photooxidation was successfully achieved in a fixed-bed, flow-through reactor that used glass beads coated with an anatase sol amended with P25. Effluent As(III) concentrations dropped from influent levels to steady-state concentrations within 8–15 min of irradiation and remained at those values even after 24 hours reaction time or 7 uses of the same batch of beads. This permitted modeling of steady-state effluent As(III) using a reactive transport model in which rate constants for As(III) oxidation were proportional to the photon flux incident at each of the 6 bead layers. As(III) sorption to

TiO_2 during the dark equilibrium period and effluent As(V) concentrations, however, were affected by increasing sorption saturation due to repeated or extended bead usage. Although these 2 parameters could not be readily modeled, they are not required for the application of this technology as a pre-oxidation step for As(III) prior to As(V) removal.

The number of TiO_2 coatings (1, 4, or 8) had no impact on steady-state effluent As(III) concentrations. Influent synthetic groundwater solutions (with or without elevated phosphate and sulfate levels) resulted in a lower reaction efficiency compared to 5 mM $NaNO_3$ solutions, probably due to sorption competition. Even so, no catalyst poisoning was observed over extended reaction time or multiple bead uses. The reaction proceeded more completely under natural sunlight than under 365 nm UV light irradiation, most likely because the flux of photons with sufficient energy to excite TiO_2 was about two times higher.

Seventy percent of influent As(III) was oxidized in the flow-through reactor when influent As was low (0.56 μM). Slight decreases in reactivity were observed as influent As(III) concentration increased to 8.3 μM; this was attributed to a shift from pseudo first-order to pseudo zero-order kinetics similar to that described in the mechanistic studies. However, the current reaction efficiency is not ideal for water treatment applications because near-complete oxidation is desired. This could be achieved by modifying the reactor geometry to make the time spent in the reactor more uniform and to implement more effective use of the reactor volume.

7.1.3 Trace As detection

Arsenic detection limits for the batch and flow-through studies summarized above were 3.3 nM, or 0.25 μg L^{-1}. This is significantly lower than the average method detection limit for ICP-MS (1.4 μg L^{-1}), primarily because the samples evaluated in this research did not suffer from chloride interference. In water treatment applications, however, chloride can be present at concentrations high enough for $^{40}Ar^{35}Cl$ to interfere with the mass spectrometry signal for ^{75}As, thus raising the analytical detection limit. Work with high resolution ICP-MS demonstrated that As can be quantified down to 29 ng L^{-1} in the presence of 35.5 mg L^{-1} chloride, with the As signal increasing nonlinearly as chloride concentration was increased to 355 mg L^{-1}. This nonlinear behavior emphasizes the need to use standard addition to quantify As in samples with unknown chloride concentration, as was demonstrated with 3 bottled waters and a tap water sample.

In addition to high resolution ICP-MS, other modified mass spectrometry technologies with very low detection limits for As are gaining in popularity. As use of such instruments becomes more widespread, the practical quantitation limit for As will decrease. This could lead to lower reporting levels and possibly to a new revision of the As maximum contaminant level.

7.2 Environmental and Human Health Implications

Removal of As from drinking water will result in fewer cancer deaths and decreased incidence of As-related morbidity. The new maximum contaminant level is projected to reduce bladder and lung cancer by more than 47 cases per year, about 26 of which would result in death (US EPA 2002b). If TiO_2 photocatalysis can be coupled with a simple sorption technique for As(V) removal, its application in developing countries like Bangladesh will have considerably greater impact due to the higher As concentrations present in the groundwater of affected regions.

TiO_2-photocatalyzed As(III) oxidation offers environmental and health benefits compared to other As pre-oxidation technologies. Chlorination, the pre-oxidation method currently used by most small groundwater systems, involves the handling of toxic chemicals and the generation of harmful disinfection byproducts. In contrast, the TiO_2 system involves no hazardous chemicals and generates no toxic reaction byproducts, resulting in an environmentally benign method of As(III) pre-oxidation.

7.3 Suggestions for Future Research

7.3.1 Mechanism of As(III) photooxidation

The mechanism of TiO_2-photocatalyzed As(III) oxidation remains an issue of considerable controversy despite several recent studies on the topic. One useful contribution to this debate would involve photooxidizing As(III) in the presence of a variety of hydroxyl radical and hole scavengers and monitoring oxidation of both the scavenger compound and As(III) concurrently. This would facilitate a quantitative analysis of the photooxidation reaction and establish whether As(III) and the quenching compound are competing for the same oxidant.

Although many approaches have been taken to elucidate the As(III) oxidation mechanism both in this study and elsewhere, most of these tactics affect the TiO_2 surface and could therefore alter the normal oxidation mechanism. Since it appears that both hole- and electron-initiated pathways lead to As(III) oxidation, outcompeting one mechanism is likely to enhance the other because of reduced recombination. Approaches such as the platinization or fluorination of the TiO_2 surface could have even more profound effects on the mechanism. An alternative approach that could minimize changes to the TiO_2 surface would employ an electrochemical cell using a thin particulate P25 film on conducting glass (Vinodgopal et al. 1993; Vinodgopal et al. 1994; Kesselman et al. 1997a). Applying an external anodic bias would favor hydroxyl radical- or hole-mediated reactions compared to the zero applied potential condition, whereas a superoxide-mediated reaction would be favored by a cathodic bias. These experiments could also be performed in the dark so that the conduction band (anodic bias) or valence band (cathodic bias) is not involved in the reaction at all (Kesselman et al. 1997b). Moreover, during the anodic bias experiment, As(III) oxidation due to superoxide production at the auxiliary electrode could be investigated.

7.3.2 Flow-through experiments and extension to pilot study

Flow-through experiments have demonstrated that a fixed-bed TiO_2 photocatalysis system has potential to be an effective method for As(III) pre-oxidation in water distribution facilities. The most outstanding need in this area is to establish whether the lack of catalyst poisoning observed in 24-hour experiments extends to significantly longer time periods, as technologies suitable for application in water treatment typically require infrequent catalyst regeneration or replacement. Also, experiments in this work were performed under air-saturated conditions, but most groundwaters containing As(III) have very low dissolved oxygen concentrations. Further experiments using a mix of N_2 and O_2 to achieve a range of low dissolved oxygen levels are needed to characterize the dependence of As(III) photooxidation on dissolved oxygen concentration. These data are critical to choosing appropriate aeration methods for anoxic source waters. If these results are promising, then the alternative reactor geometry described in Chapter 6 could be tested and expanded into a pilot study.