Photocatalytic Adsorption Media and Processes for Enhanced Removal of Arsenic from Groundwaters

Project Completion Report

University of Wisconsin Water Resources Institute
Wisconsin Groundwater Research Program

Project # R/UW-WSP-001

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Project Summary

Title:	**Photocatalytic Adsorption Media and Processes for Enhanced Removal of Arsenic from Groundwaters**

Project I.D.:   **R/UW-WSP-001**

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Publications

1. E. Lee, M.A. Anderson, W.A. Zeltner, Arsenic Removal Strategies Using Novel Adsorbent Material, American Water Works Association 2003 Annual Conference, Proceeding Paper, Anaheim, Ca., 6/15 – 6/19/2003.

2. E. Lee, M.A. Anderson, W.A. Zeltner, Photoactive Removal of As (III) From Water Using Novel Active Material, American Water Works Association 2003 Annual Conference, Proceeding Paper, Anaheim, Ca., 6/15 – 6/19/2003.

Objectives:

The main objective of this study is to validate the new technologies we have developed in our laboratory for arsenic removal and to develop parameters for scaling these techniques to use in the field.

Methods:

Aluminum oxide (Al_2O_3), spinel ($MgAl_2O_4$), titanium dioxide (TiO_2) and mixed sols were synthesized by sol-gel technology and coated on glass beads. The synthesized media were tested in batch, column, and differential column batch reactors using synthetic solutions and groundwater samples from Danvers, Ill.

Results and Discussions:

Many arsenic removal processes have been found to be ineffective for arsenite, As(III), which is uncharged at the pH of drinking water. Removal of As(III) is generally accomplished by oxidizing it to arsenate, As(V), which can be removed by adsorption or ion-exchange mechanisms.

Previous researchers have found that the TiO_2/ultraviolet photocatalytic process effectively converts As(III) to As(V). However, most of these studies were performed with TiO_2 nano-particle suspensions. Removal of these particles later in the treatment process could be problematic. During the authors' testing, a heterogeneous photocatalytic adsorbent (Al_2O_3/TiO_2) was synthesized by sol-gel techniques and shown to effectively remove As(III) without requiring a separate oxidation process. This composite acts as a photocatalyst that can oxidize As(III) to As(V), with the latter species being adsorbed by the adsorbent. The materials (Al_2O_3/TiO_2) were mixed as a stable suspension (sol) that was used to coat glass beads. After the coated beads were fired, the resulting thin films served as both a photocatalyst and an adsorbent. It was found that the TiO_2 photocatalyst oxidizes As(III) at the same rate at a lower dissolved oxygen DO level (~ 1 mg/L) as at a higher DO level (7 mg/L).

Conclusions/ Implications/ Recommendations:

This study indicates that photocatalytic adsorption may prove to be an effective single-step method for removing arsenite without requiring separate oxidation and adsorption processes. Mixed coated media have been shown to remove arsenite more effectively than either pure Al_2O_3 or TiO_2. Photocatalytic oxidation of arsenite was found to be effective for both synthetic solutions and groundwater samples from Danvers, Ill. The photooxidation rate was not changed at a lower dissolved oxygen level, and the rate of arsenite oxidation in synthetic solutions and in groundwater samples was comparable. The photooxidation rate was not changed even after 6000 hours operation without regeneration. Arsenic adsorption on the surface of the photocatalyst did not interfere with the arsenite oxidation rate, therefore, this device is possible to use as a photocatalytic adsorption process. This test shows the potential for this combined oxidation-adsorption process, although further development and optimization is required.

Related Publications: None at present.

Key Words: Arsenite, Arsenate, Adsorption, Surface Charge, Photooxidation, Arsenic Remediation

Funding: University of Wisconsin Water Resources Institute

Introduction

Arsenic is widely distributed in the environment, generally at low concentrations. Inorganic arsenic is often combined with one or more other elements such as oxygen, chlorine, and sulfur [1]. Arsenic was one of the first chemicals to be considered as a carcinogen [2]. Previous studies correlated low level concentrations of arsenic in drinking water with deaths resulting from bladder and lung cancer [3]. The combined cancer mortality risk was found to be as high as 1 in 100 for people drinking water that contained 50 µg/L of arsenic [4, 5] and 1 in 10 for 500 µg/L [6, 7].

The four possible oxidation states for arsenic are arsenate [As(V)], arsenite [As(III)], arsenic [As(0)], and arsine [As(-III)]. However, the As(V) and As(III) forms are most common in natural waters [8], with the ratio of the concentrations of the two species controlled primarily by the redox state (E_h) and the pH of the solution.

As(III) dominates under anaerobic conditions or when reducing agents are present, while As(V) dominates under oxidizing conditions. As(III) exists in solution as neutral arsenious acid until the pH approaches 9.22, the first pK of this acid. As(V) has three pK values (2.66; 6.77; 11.50) and is mainly present as an anion (charged either –1 or –2) in drinking water.

An understanding of these arsenic oxidation and reduction reactions is essential to the treatment of arsenic in water because the oxidation status of arsenic significantly influences the efficiency of arsenic removal. As(III) is considered harder to remove than As(V) since As(III) is uncharged at the typical pH of natural water [9]. As a result, there is little electrostatic attraction to drive adsorption of As(III) onto positively charged media such as activated alumina or hydrous ferric hydroxide. For similar reasons, ion exchange [10] and conventional coagulation filtration processes [11] were also found to be ineffective in removing As(III).

Because groundwater is often under anoxic conditions, the proportion of As(III) to As(V) in groundwater is relatively higher than in surface waters. As(III) also dominates when strong reducing agents are present [1]. In Bangladesh, where arsenic problems have been severe, As(III)/As(V) ratios vary between 0.1 ~ 0.9. In Mongolia, this ratio is 0.7 ~ 0.9 [1]. In the US, only limited studies have been performed to determine this ratio. Recently, Johnson et al [12] reported a value near unity (As(III)/As(V) ≈ 1.0) for groundwater in the Fox River Valley area in Wisconsin.

To remove As(III) an additional preoxidation stage is usually employed to convert As(III) to As(V) [13]. Previous research found that chemical oxidants including chlorine, ozone, and permanganate were effective in converting As(III) to As(V) [13]. A solid phase media, which contain 75 ~ 85% of manganese dioxide, was also found to be useful [14]. Except in the manganese dioxide oxidation process, most of these processes involve the chemical addition of oxidants. These chemical oxidation processes are difficult to use in small communities that cannot easily handle these chemical oxidants properly and even greater safety issues may likely surface. These oxidation processes will increase both the construction and operating costs for arsenic treatment as well.

To remove As(III), one typically utilizes a prior oxidization step to convert As(III) to As(V), followed by adsorption of As(V). There have been several attempts to simplify this treatment process by removing both arsenic species in a single step (i.e., combined sorption and oxidation).

Raven et al. claimed that ferrihydrite adsorbs even more As(III) than As(V) under most ranges of pH [15]. This research was performed with extremely high initial concentrations of arsenic (40 mg/L ~ 2,000 mg/L).

In a relatively recent patent, Khoe et al. developed the use of UV light to oxidize As(III) to As(V). Khoe et al. claim that photo-assisted oxidation using UV light effectively converts As(III) to As(V) [16]. However, Ghyrie and Clifford's pilot study found that UV oxidation was only effective at extremely high UV intensities (7,000 times the UV dose required for E. Coli inactivation) [13]. Ghyrie and Clifford conducted their pilot test with 200 nm UV light. Even though Khoe et al. claim that UV oxidation is effective at higher wavelengths (> 300 nm), Bissen et al. reported that only 54% of As(III) oxidized in 45 minutes [17].

Recently, TiO_2-catalyzed photooxidation of As(III) to As(V) has been studied [18]. UV oxidation occurs when the energy from UV light is transferred directly to the reaction. In contrast, TiO_2 oxidation utilizes a semiconducting photocatalyst in a process that has been shown to effectively remove organic contaminants in water systems [19]. In this process, the photocatalytic TiO_2 absorbs light having energy greater than the band gap energy of the TiO_2 (about 3.2 eV or 380 nm light), producing electrons and holes on the surface of the oxide. The strongly oxidizing holes break down organic contaminants and can also convert As(III) to As(V) [18]. Lee and Choi observed that photooxidation/adsorption by suspensions of TiO_2 effectively removed As(III) [18]. Bissen et al [17] demonstrated that nanoparticulate suspensions of TiO_2 illuminated with UV light can oxidize As(III) to As(V) in less than three minutes, although it can be difficult after treatment to separate the treated solution and the particulate TiO_2 photocatalyst [18]. An alternative approach is to immobilize the TiO_2 by coating it on a substrate. Using a TiO_2-coated media may be an excellent arsenic removal scenario.

Even though TiO_2 gel can adsorb significant amounts of arsenic [20], a mixed oxide consisting of Al_2O_3 and TiO_2 may increase arsenic adsorption since γ-Al_2O_3 is a better adsorbent than TiO_2. In addition, adsorption of arsenic on the TiO_2 might inhibit the activity of the TiO_2 photocatalyst. The mixed oxide system was studied as a method that might allow effective photooxidation-adsorption to occur in one step.

Materials and Methods

Preparation of γ-Alumina Sol: Adsorbents for this study were prepared by the sol-gel process, which basically involves the transition of a system from a liquid "sol" (i.e., stable suspension) into a solid "gel" phase. Pure gamma alumina (γ-Al_2O_3) was prepared from a precursor boehmite (AlOOH) sol that was synthesized by sol-gel techniques as described by Yoldas [23]. Aluminum tri-sec-butoxide [$Al(OC_4H_9)_3$ ATSB] (Aldrich Chemical, Milwaukee, Wis.) was hydrolyzed by heating water to $80 - 85$°C and adding a 2.0 M ATSB solution (in 2- butanol) to give a 100:1 molar ratio of water to ATSB. After stirring for 1-2 h, 1.6 M nitric acid was added to the hydrolyzed ATSB (enough acid to give a 1:14 molar ratio of HNO_3 to ATSB) to keep the pH of the solution at 4.0 throughout this high temperature hydrolysis. After an additional hour of

stirring, the 2-butanol/water azeotrope was boiled off. Particle size in the resulting sol was ca. 20 nm. The prepared AlOOH converts into γ-Al$_2$O$_3$ between 90°C and 475 °C [23]. Therefore, most of the AlOOH was assumed to convert to γ-Al$_2$O$_3$ during calcination at 350 °C for three hours.

Preparation of Titania Sol: While 5,000 mL of 0.1 N nitric acid was stirred, 417 ml of titanium isopropoxide was added slowly. The addition immediately gave a cloudy white suspension. The suspension was continuously stirred for 3-4 days to peptize (i.e., break up) the suspension and formed a slightly cloudy, bluish sol. In order to obtain a coating with a high porosity, the sol was dialyzed after peptization. The dialysis process increases the pH of the sol to the desired value, thereby reducing electrostatic repulsion forces between colloidal particles in the sol and allowing the particles to aggregate slightly. Spectra/Por® dialysis tubing with a flat width of 54 mm and a molecular weight cutoff of 3,500 was employed (Spectrum Companies, (Gardena, Cal.). Prior to use, the tubing was washed in an aqueous solution of 0.001 M EDTA and 2% (w/w) sodium bicarbonate. The wash solution was prepared by dissolving 10 ml of 0.0990 M EDTA solution (Aldrich Chemical, Milwaukee, Wis.) and 43 grams of sodium bicarbonate powder (Aldrich Chemical, Milwaukee, Wis.) in one liter of ultra-pure water. The dialysis tubing was cut into sections 32 cm in length and then submerged in the wash solution. The solution was heated to 80°C and held for 30 minutes while the sections of tubing were stirred. After the solution cooled, the tubing was rinsed with ultra-pure water. This process was repeated, substituting ultra-pure water for the wash solution. The cleaned tubing was stored in ultra-pure water at 4°C until needed.

Dialysis was performed by placing ca. 300 mL of the peptized sol in a piece of tubing sealed at one end with a polypropylene clip. After filling, the other end of the tubing was sealed with another polypropylene clip. The tubing containing the sol was submerged in ultra-pure water using a ratio of 100 mL of sol per one liter of ultra-pure water. The sol was dialyzed 3-4 days until a final pH of 3.5 was reached. Note that the ultra-pure water used in this dialysis was changed daily. The dialyzed sol can be refrigerated and stored until needed.

Coating: For the batch tests, 6 × 6 mm glass Raschig rings were coated with both adsorbents using dip-coating techniques. Therefore, both adsorbents had identical geometric surface areas and shapes. Before coating, the rings were calcined at 550°C to remove the organic matter on the surface, after which the rings were base treated by dipping into 0.1 M NaOH for more than eight hours. After rinsing with water, these base-treated rings were coated with sols obtained by mixing the TiO$_2$ and AlOOH precursor sols at selected ratios. The rings were withdrawn from the sols at a rate of 25 cm/min and allowed to air dry under ambient conditions. After air drying, the coated rings were calcined at 350°C for three hours to form the nanoporous xerogel film.

Characterization of Materials: Specific surface areas of the adsorbents were measured with an ASAP 2010 micropore analyzer (Micromeritics Inc., Norcross, Ga.), using a BET analysis of N$_2$ gas sorption data at liquid N$_2$ temperatures [24]. Before measuring surface areas, gaseous adsorbates were removed by heating the adsorbents at 120°C for about 2 h under vacuum. Specific surface areas of the xerogels were 330 m^2/g for γ-alumina and 200 m^2/g for titanium dioxide (TiO$_2$). The surface area of adsorbent coated on the glass rings was estimated based on the amount of coated material deposited on the media (glass rings). To measure the amount of

material coating each glass ring, 100 g of media was dip coated with the 1:1 by volume mixed oxide sol and air dried. The air dried media was put into 200 mL of 10% HCl overnight to dissolve the coated alumina and TiO_2. After the rings were removed, they were rinsed several times with ultra-pure water to remove as much dissolved alumina and titania as possible. The rinse and acid-digestion solutions were combined and diluted with ultra-pure water to a volume of 238 mL in a graduated cylinder. Fifty mL of this solution was transferred to a volumetric flask. The concentration of aluminum in this solution was measured by inductively coupled plasma – atomic emission spectroscopy (ICP-AES), and this concentration was used to estimate the mass of material dissolved off of the rings. The surface area of the adsorbent on the glass rings was estimated based on the surface area of the xerogel material. Specific surface areas of the coated glass media were similar regardless of the Al/Ti ratio. The estimated surface area of the coated glass media ranged from $0.18 \sim 0.19$ m^2/g.

Particle sizes and zeta potentials were measured using a Malvern Instruments (Southborough, MA) Zetasizer 3000. Latex particle size (supplied by Duke Scientific) and zeta potential (supplied by Malvern) standards were used to verify instrument performance. Zeta potential standards with an accepted value of -50 mV were injected before measurements and a $\pm$ 10% error margin was accepted. Zeta potential measurements were conducted with and without arsenate but always using a 0.01 M $NaNO_3$ background electrolyte. Enough arsenate was added to the samples to maintain a fixed ratio of 164 μg of arsenate per m^2 of adsorbent (as the powdered xerogel). Sample pH was adjusted with 0.1 M NaOH and HNO_3 to obtain the desired pH for the measurement.

Performance of Adsorption Experiments: All solutions for this study were prepared using ultra-pure water obtained from a Barnstead (Dubuque, Ia.) NANOpure UV purification system. All glassware was cleaned by soaking in 10% HCl and rinsed four times with deionized water. The 0.1 N sodium arsenite standard solution, $NaAsO_2$ (Alfa Aesar), was used as stock solution. Total arsenic concentrations were determined by ICP-AES using a Perkin Elmer (Norwalk, Conn.) Optima 4300 set at 188.975 nm wavelength. A certified ICP standard solution containing 1,000 mg As/L (Spex Certi Prep. Inc., Metuchen, NJ) was used to prepare all calibration solutions.

Arsenic Speciation: Strong Anion Exchange cartridges, (SAX, 3 mL, Supelco, Bellefonte, Pa.) were used to separate As(III) from arsenic solutions. A MasterFlex Pump (Cole-Parmer, Chicago, Ill.) was used to pass 10 mL of sampled solution through the cartridge at a flow rate of ca. 1.5-2.0 mL/min. Filtered sample contained As (III) while unfiltered samples contained total arsenic. The amount of As(V) was calculated by subtracting As(III) from total arsenic. The concentrations of both As(III) and total arsenic were determined by ICP-AES.

Batch Test: Each batch adsorption experiment employed approximately 2 g of the supported adsorbent (10 coated glass rings) to which was added 30 mL of the arsenate stock solution in a large Pyrex® Petri dish. The light source was a 15-watt Sylvania UV blacklight (F8T5/350BL) that emits at an average wavelength of 360 nm. Pyrex glass transmits more than 95% of 360-nm UV light while it cuts off wavelengths less than 300 nm. The initial solutions contained 1,000 ppb of As(III) at pH 7.0. These amounts allowed us to maintain the ratio of adsorbate to adsorbent in the range of 164 ± 5 μg/m^2 for both adsorbents. The pH of the solution was adjusted with 0.1 M NaOH and HNO_3.

Column Test: A Pyrex® glass column (20 mm length × 170 mm in diameter, 53 ml in volume) was used for this column test and illuminated from the outside. The light sources were four Sylvania 350 Blacklight bulbs (F15T8/350BL, 15 watt each). The reactor was packed with 19 g of coated media obtained using a sol with TiO_2 only or a mole ratio of TiO_2/Al_2O_3 of 0.38. The available volume of the reactor when packed with the media was 53 mL. Source water was pumped into the column at a rate of 10 mL/min, giving an empty bed contact time (EBCT) of approximately five minutes.

Differential Column Batch Reactor (DCBR): The column test setting was modified for the DCBR test. After adjusting pH and desired initial concentration of arsenic in the reservoir (1 L), solution was pumped into the prepared column at a rate of 10 mL/min (EBCT ≈ 5 min) and treated solution was recirculated to the reservoir. Periodically, 2 mL of solution was sampled from the reservoir and diluted with 20 mL of ultra-pure water. Some 10 mL of sampled solution was filtered with SAX to remove any As(V) that formed and thus to determine the concentration of As(III) while the other 10 mL of sampled solution was analyzed to determine the total arsenic concentration. Concentrations of arsenic in these samples were determined by ICP-AES.

Results and Discussion

Batch Test: Figure 1 depicts the fraction of arsenic that was removed from the solution in the batch reactor. The concentration of arsenic was measured before and after adsorption on glass rings that were coated with mixed oxide sols containing different TiO_2/Al_2O_3 ratios. The optimum TiO_2/Al_2O_3 mole ratio was found to be 0.6 ~ 0.7. Media coated with pure Al_2O_3 and TiO_2 removed only 25% and 61% of As(III), respectively, while media coated with the optimum TiO_2/Al_2O_3 ratio of 0.69 removed 95% of As(III) in the 10-minute reaction time under UV illumination. These results demonstrate the effectiveness of this approach as a method for treating As(III).
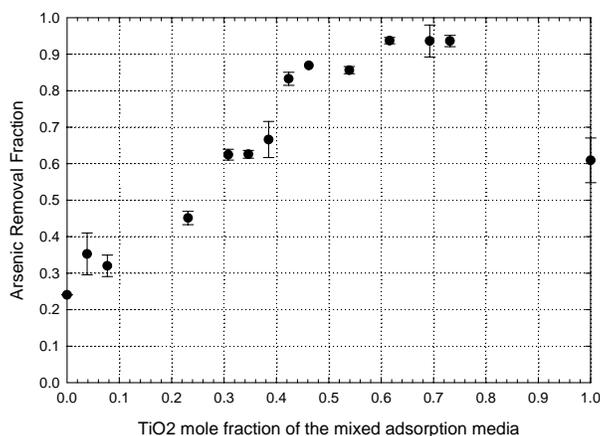

Figure 1. Arsenic removal fraction after 10 minutes of UV illumination (initial arsenite concentration of 1,000 ppb).

Column Test: A series of column tests were conducted to determine the best flow rate for the prepared column packed with the optimized photocatalyst. The reactor was operated for four hours at each EBCT and samples were collected hourly. Data in Figure 2 show that the optimal EBCT is 10 minutes with ca. 80% of arsenite oxidized in this batch reactor. (The arsenite oxidation rate may change depending on the size and shape of the reactor.) A column test was conducted for 900 minutes, as shown in Figure 3, using a test solution containing ca. 100 µg/L of As(III) and a flow rate of 5 ml/min (EBCT = 10 min). At the start of this test, the concentrations of both total arsenic and As(III) in the outflow were around 20 µg/L, indicating that about 80% of As(III) had oxidized and adsorbed onto the surface of the media. The total arsenic concentration in the outflow increased as the capacity of the photocatalytic adsorption medium was used up. However, the concentration of As(III) in the outflow remained constant for the entire 900-minute operation, suggesting that the oxidation rate was stable despite the adsorption of arsenic on the photocatalyst/adsorbent.
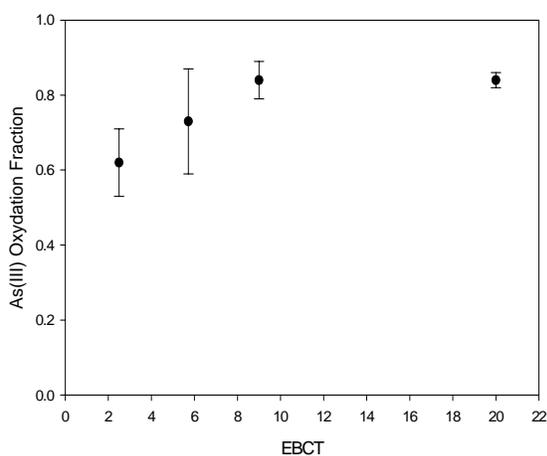

Figure 2. Fraction of arsenite oxidized at different EBCTs using the optimum TiO_2-coated medium. (Initial concentration of As(III) 200 µg/L; pH 7.0)

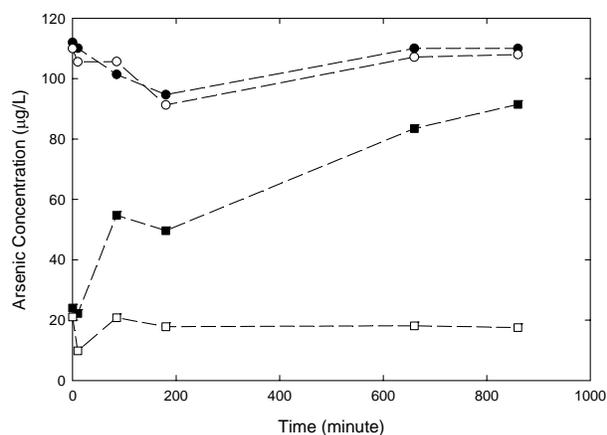**Figure 3.** As(III) oxidation and adsorption onto a mixed TiO_2/Al_2O_3 medium over a 900-minute period in the presence of UV light. (Initial concentration of arsenite 100 µg/L; pH 7.0; (●) inflow total As, (○) inflow As(III), (■) outflow total As, (□) outflow As(III))

Differential Column Batch Reactor (DCBR): The DCBR was prepared by using the packed column described above but without connecting it to the reservoir and the recirculation pump. This reactor was employed to determine oxidation rates for both synthetic solutions and groundwater samples from Danvers, Ill. Figure 4 depicts the results of DCBR tests for solutions consisting of 2 mg/L As(III) in 0.01 M $NaNO_3$ and illuminated with UV light for 10 hours. After each test, the solution in the reactor was drained, replaced with fresh solution, and the test was repeated without changing the photocatalyst (TiO_2/Al_2O_3) medium. As shown in this figure, the oxidation rates between the first and tenth batches are comparable. These data suggest that the

rate of arsenite oxidation over this photocatalyst does not change even when the reactor is operated for almost 100 hours (6,000 minutes) without regenerating the catalyst.

The DCBR was also operated with groundwater samples from Danvers, Ill. To prepare the test solution, the groundwater samples were prefiltered with a 0.45-μm membrane filter and an extra 2 mg of arsenite was spiked into every 1 L of sample. Each batch test was performed for five hours, giving a total operation time of ca. 50 hours. As shown in Figure 5, the oxidation rate was not significantly changed between the first and tenth batch. Since the dissolved oxygen (DO) level of groundwater from Danvers is typically 1 mg/L or less, the DCBR was also operated at lower DO level (~ 1 mg/L). (This variable is important because DO acts as an electron acceptor during the photooxidation process.) To lower the oxygen level in the solution, nitrogen (N_2) gas was purged during the test. During nitrogen purging, the DO level was stable at 1 mg/L, whereas without purging the DO level was stable at 7 mg/L. (DO levels were measured using a YSI (Yellow Springs, Ohio) Model 58 DO meter.) As shown in Figure 5, the arsenite oxidation rate was similar at both DO levels. The test data in Figure 5 suggest that 1 mg/L of oxygen (0.031 mM) may be sufficient to oxidize 2 mg/L (0.027 mM) arsenite, although the relatively high concentration of iron in the source water (3 mg/L, 0.054 mM) may allow iron to act as an electron acceptor as well. Typical concentrations of As(III) in real groundwater samples are generally only 20 ~ 40 μg/L. Therefore, the existing 1 mg/L of oxygen in groundwaters should be sufficient to oxidize this amount of arsenite without the need to add extra oxygen to support the photooxidation process.

Compared to the synthetic solutions, the groundwater samples from Danvers, Ill. display a slightly slower oxidation rate. This difference may result from some absorption of the UV light by the groundwater samples, which are colored brown because of the high levels of iron that are present. A decrease in the intensity of light that strikes the photocatalyst should lower the rate of oxidation that is observed.

Conclusions

Arsenite, As(III), is regarded as a harder species to remove than arsenate, As(V), since arsenite is uncharged over the pH range of natural water (6.0~9.0). This study indicates that photocatalytic adsorption may be an effective single-step method for removing arsenite without requiring separate oxidation and adsorption processes. Mixed coated media have been shown to remove arsenite more effectively than either pure Al_2O_3 or TiO_2. This test shows the potential for this combined oxidation-adsorption process, although further development and optimization is required.
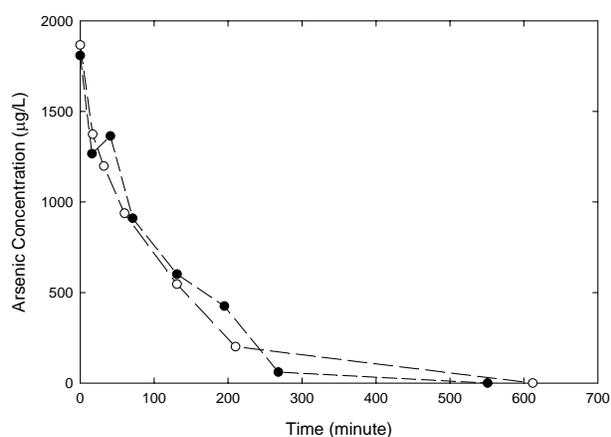
Figure 4. Comparison of As(III) concentration changes in synthetic solutions containing 0.01 M NaNO$_3$. (Initial concentration of arsenite 2000 µg/L; pH 7.0; DO 7 mg/L; EBCT 10 minutes; (●) first batch, (○) tenth batch)

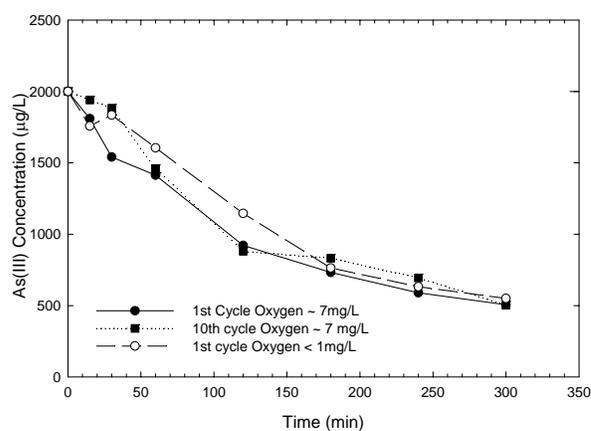**Figure 5.** Comparison of As(III) concentration changes in groundwater samples from Danvers, Ill. (Initial concentration of arsenite 100 µg/L; pH 7.0; EBCT 10 minutes; (●) first batch at 7 mg/L DO, (■) tenth batch at 7 mg/L DO, (○) first batch at 1 mg/L)
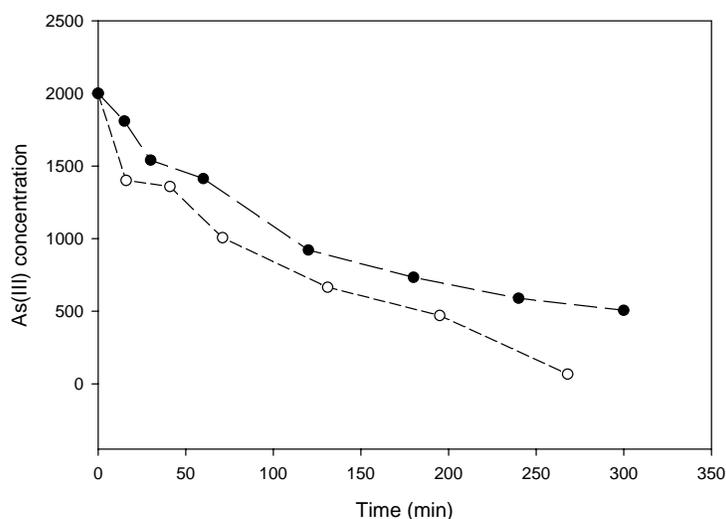

Figure 6. Comparison of As(III) concentration changes between a synthetic solution containing 0.01 M NaNO$_3$ and a groundwater sample from Danvers, Ill. spiked with As(III). (Initial concentration of arsenite 2000 µg/L; pH 7.0; DO 7 mg/L; EBCT 10 minutes; (●) groundwater sample from Danvers, IL, (○) synthetic solution)

References

1. Smedley, P.L. and D.G. Kinniburgh, *A review of the source, behaviour and distribution of arsenic in natural waters.* Applied Geochemistry, 2002. **17**(5): p. 517-568.
2. Smith, A.H., et al., *Public health - Arsenic epidemiology and drinking water standards.* Science, 2002. **296**(5576): p. 2145-2146.
3. Frost, F.J., et al., *Physical injury risks associated with drinking water arsenic treatment.* Risk Analysis, 2002. **22**(2): p. 235-243.
4. Smith, A.H., et al., *Cancer Risks from Arsenic in Drinking-Water.* Environmental Health Perspectives, 1992. **97**: p. 259-267.
5. Smith, A.H., et al., *Arsenic Risk Assessment.* Environmental Health Perspectives, 1995. **103**(1): p. 13-15.
6. NRC, *Arsenic in Drinking Water 2001 Update.* National Research Council, 2001.
7. Saha, J.C., et al., *A review of arsenic poisoning and its effects on human health.* Critical Reviews in Environmental Science and Technology, 1999. **29**(3): p. 281-313.
8. Cullen, W.R. and K.J. Reimer, *Arsenic Speciation in the Environment.* Chemical Reviews, 1989. **89**(4): p. 713-764.
9. Clifford, D. and C. Lin, *Arsenic (III) and Arsenic (V) Removal From Drinking Water in San Ysidro, New Mexico.* 1985, EPA: Cincinnati, Ohio.
10. Wang, L., A. Chen, and K. Fields, *Arsenic Removal from Drinking Water by Ion Exchange and Activated Alumina Plants.* 2000.
11. Chen, P., *Speciation and Matrix Effects on Arsenic Removal by Coagulation with Ferric Chloride and Alum.* 1996, University of California - Los Angeles: Los Angeles, Ca.
12. Johnson, R.L. and J.H. Aldstadt, *Quantitative trace-level speciation of arsenite and arsenate in drinking water by ion chromatography.* Analyst, 2002. **127**(10): p. 1305-1311.
13. Ghyrie, G. and C. D., *Laboratory Study on the Oxidation of Arsenic III to Arsenic V.* 2001, EPA.
14. Amy, G., *Arsenic Treatability Options and Evaluation of Residuals Management Issues*, AWWARF: Denver, Colo.
15. Raven, K.P., A. Jain, and R.H. Loeppert, *Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes.* Environmental Science & Technology, 1998. **32**(3): p. 344-349.
16. Khoe, G.H., E. M.T., and R. R.G., *Photoassisted oxidation of species in solution.* 1997: U.S.
17. Bissen, M., et al., *TiO2-catalyzed photooxidation of arsenite to arsenate in aqueous samples.* Chemosphere, 2001. **44**(4): p. 751-757.
18. Lee, H. and W. Choi, *Photocatalytic oxidation of arsenite in TiO2 suspension: Kinetics and mechanisms.* Environmental Science & Technology, 2002. **36**(17): p. 3872-3878.
19. Hoffmann, M.R., et al., *Environmental Applications of Semiconductor Photocatalysis.* Chemical Reviews, 1995. **95**(1): p. 69-96.
20. Liang, S., et al., *Nitrate removal from contaminated groundwater.* Journal American Water Works Association, 1999. **91**(2): p. 79-91.

APPENDIX A

Presentations:

1. Marc Anderson, Eunkyu Lee, Isabel Tejedor, and Tom Holm, Photoactive removal of As(III) from water using novel active material, 226th American Chemical Society National Meeting, New York, N.Y., Oral Presentation, September 7–11, 2003.

2. Eunkyu Lee, M. Anderson, and W. Zeltner, Arsenic Removal Strategies Using Novel Adsorbent Material, American Water Works Association 2003 Annual Conference, Proceeding Paper, Anaheim, Cal., June 15-19, 2003.

3. Eunkyu Lee, M. Anderson, W. Zeltner, Photoactive Removal of As(III) From Water Using Novel Active Material, American Water Works Association 2003 Annual Conference, Proceeding Paper, Anaheim, Cal., June 15-19, 2003.

4. Eunkyu Lee, M. Anderson, and W. Zeltner, Arsenic Removal Strategies Using Novel Adsorbent Material, 25th Midwest Environmental Chemistry Workshop, Chicago, Ill., Oral Presentation, October 5, 2002.

5. M. Anderson, Eunkyu Lee, and Isabel Tejedor, Photoactive Removal of As(III) from Water using Novel Al/Ti Active Material, 25th Midwest Environmental Chemistry Workshop, Chicago, Ill., Oral Presentation, October 5, 2002.