

# Removal of As(III) and As(V) in contaminated groundwater with thin-film microporous oxide adsorbents. 2002

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# Removal of As(III) and As(V) in Contaminated Groundwater with Thin-film Microporous Oxide Adsorbents

Marc A. Anderson (P.I.) Walt Zeltner Eunkyu Lee

2002

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**Project Completion Report** 

# University of Wisconsin Water Resources Institute Groundwater Research Project

# Marc A. Anderson (P.I.) Walt Zeltner

Eunkyu Lee

# Environmental Chemistry and Technology Program University of Wisconsin – Madison

This project was supported, in part, by General Purpose Revenue funds of the State of Wisconsin to the University of Wisconsin System for the performance of research on groundwater quality and quantity. Selection of projects was conducted on a competitive basis through a joint solicitation from the University and the Wisconsin Departments of Natural Resources; Agriculture, Trade and Consumer Protection; Commerce; and advice of the Wisconsin Groundwater Research Advisory Council and with the concurrence of the Wisconsin Groundwater Coordinating Council.

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### **Project Summary**

Title:	Removal of As(III) and As(V) in Contaminated Groundwater with Thin- film Microporous Oxide Adsorbents				
Project I.D.:	R/UW-REM-003				
Investigators:	Marc A. Anderson (Principal Investigator) Professor, Environmental Chemistry and Technology Program University of Wisconsin – Madison				
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**Period of Contract:** July 2000 – June 2002

#### **Objectives:**

The principal objective of this study is to develop and test inexpensive, high-performance photoactive adsorption media for the simultaneous removal of arsenite, As(III), and arsenate, As(V), from groundwater without pH adjustment. This process utilizes UV-irradiated photoactive thin films composed of novel mixed oxides prepared by sol-gel processing. These materials will be employed in a unique photocatalytic process, which simultaneously removes both arsenic species without additional pH adjustment or further chemical addition.

#### **Methods:**

Aluminum oxide  $(Al_2O_3)$ , spinel  $(MgAl_2O_4)$ , and titanium oxide  $(TiO_2)$  sols were synthesized by sol-gel technology and coated on glass beads. The adsorption efficiency of each coated material was determined in a batch reactor.

#### **Results and Discussions:**

The relationship between the adsorption capacity and the pH of the isoelectric point (IEP) of aluminum oxide and spinel was intensively studied. The IEP of pure aluminum oxide was 8.0, but its IEP decreases to 5.4 when it adsorbs arsenic. Pure spinel had a higher IEP of 10.2, which decreased to 6.7 after adsorption of arsenic. The adsorption capacity for arsenic significantly decreased for both materials at pH values higher than their IEP. These results confirm that (1) adsorption of anions shifts the IEP of adsorbents to lower pH values and (2) the IEP of the adsorbent is strongly related to its adsorption capacity.

During this research, we also developed a novel approach for simultaneously removing both As(III) and As(V) without a <u>separate</u> oxidation step. This process involves heterogeneous photocatalytic adsorption. The adsorbent acts as a photocatalyst to oxidize arsenite to arsenate with the latter species being adsorbed by the catalytic adsorbent. Our studies utilized two types of nanoparticles,  $TiO_2$  and AlOOH. These particles were mixed as a stable suspension (sol) that was used to coat glass beads. The thin-films that were deposited on the beads served as both the photocatalyst and the adsorbent. Test solutions at pH 7.0 contained 0.01 M NaNO<sub>3</sub> as a background electrolyte and initial concentrations of arsenite and arsenate of 3 mg/L in separate studies of adsorption in the presence and absence of UV light. Based on the batch tests, the amount of As (III) adsorbed onto the mixed Al+Ti medium was almost identical to that of As (V). These results suggest that almost 100% of arsenite is oxidized to arsenate with this latter species being adsorbed by the film.

#### **Conclusions/Implications/Recommendations:**

Adsorption processes that employ activated alumina require a pH between 5.5 and 6.0 for optimum arsenic removal. Because these pH values are outside the pH range at which most water treatment plants operate (pH =  $6.0 \sim 9.0$ ), most plants install a separate pH adjustment unit before the adsorption process. Results of this study indicate that the IEP of pure aluminum oxide, which is the main component of activated alumina, is 8.0. This IEP decreases to 5.4 when the aluminum oxide adsorbs arsenate. This result confirms that the pH effect noted above is likely due to the adsorption of arsenate or other protolyzable anions on the activated alumina, which lowers its IEP from 8.2 to  $5.5 \sim 6.0$ . The spinel material displays the same effect. However, because spinel has a higher intrinsic IEP than aluminum oxide, the adsorption capacity of spinel for arsenate does not decrease significantly over the typical pH range of natural waters. As a result, spinel adsorbs 2.5 times more arsenate than activated alumina at pH 7.0.

Another concern with arsenic removal is treating arsenite, which is uncharged at the pH of drinking water, therefore, difficult to remove by adsorption or ion exchange. Arsenite is typically removed by oxidizing it to arsenate and then adsorbing the arsenate. The use of a  $TiO_2$  photocatalyst has been shown to significantly accelerate the photooxidation of arsenite. Initial studies demonstrate that both arsenic species can be removed in a photocatalytic adsorption process using a novel thin-film material.

#### 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 a well-known toxic material. Generally, both acute and chronic toxicity are caused by inorganic arsenic species that can be ingested, inhaled, or absorbed through the skin and subsequently incorporated into body organs. The accumulation of arsenic in the human body may cause various diseases including cardiovascular effects and diabetes mellitus (Nagvi et al. 1994; Smedley and Kinniburgh 2001). Although the Agency for Toxic Substances and Disease Registry found these two species equally toxic (ATSDR 1993), recent studies indicate that As(III) is more toxic than As(V) (Naqvi et al. 1994). Also, arsenic is known as a carcinogen. Recent research by the National Academy of Sciences (NAS) found that the lifetime excess risk for bladder and lung cancer combined is estimated to be approximately 1 in 1,000 at 3  $\mu$ g/L arsenic and 7 in 1,000 at 20  $\mu$ g/L (Goyer 2001).

On October 31, 2001, the U.S. Environmental Protection Agency (EPA) announced that the Maximum Contaminant Level for arsenic in drinking water would be reduced from the present level of 50 ppb to 10 ppb by the year 2006. To comply with the new arsenic regulation set by EPA, many groundwater pumping stations need to install treatment units to remove excess arsenic. Nationwide costs to comply with meeting the new arsenic standard are estimated by the American Water Works Association to be approximately \$600 million annually with \$6 billion in initial capital costs. This new standard may add about \$2,000 per year for water costs to individual ratepayers if currently available techniques are used (Frey 2000).

Due to the relatively low capital cost and low operating expense of the adsorption process, adsorption technologies are likely to be the preferred method for removing arsenic in small-scale drinking water systems. Because of its low cost and high surface area, activated alumina has been the preferred adsorbent. However, the effectiveness of arsenic adsorption on activated alumina is highly dependent on pH and the oxidation state of arsenic.

Previous studies have found the optimal pH range for adsorbing As(V) on activated alumina to be in the range of 5.5 - 6.0 (Clifford and Lin 1985; Hathaway and Rubel 1987). Rosenblum and Clifford (1984) found that the adsorption capacity of activated alumina for arsenic is significantly decreased when the pH increases above ca. 5.7. This adsorption capacity was 14 times higher at pH 6.0 than at pH 7.5 (Clifford 1999).

Because these optimal pH values are lower than the typical pH of natural waters  $(6.0 \sim 9.0)$ , pH adjustment is required for optimum removal (EPA 2000a; Wang et al. 2000). Based on an economic analysis for arsenic removal processes conducted by the EPA (2000a), a pH adjustment process increases the capital cost of using activated alumina by 86% for a 1-million-gallon per day (MGD) treatment system. The same report indicated that the operation cost would be 90% higher when the source water is pH 8.0 as compared to pH 7.0 for a 1 MGD plant. There has been only limited economic analysis of arsenic treatment methods that incorporate an oxidation process to remove arsenite. However, the costs of constructing and operating such a system are likely to be even more discouraging than for pH adjustment.

Generally, activated alumina in water treatment is composed of more than 98% aluminum oxide  $(\gamma-Al_2O_3)$ . The isoelectric point (IEP) for this material is ca. 8.2 (Clifford 1999). The IEP is the pH at which positive and negative surface charges balance, leaving a neutral particle. However, this IEP is not fixed. Metal oxides react with water and develop a pH-dependent surface charge that becomes more positive as pH decreases. However, the IEP changes when protolyzable

anions such as As(V) or hydrolyzable cations such as HgOH<sup>+</sup> chemically bind to an oxide surface (Anderson 1974). For example, the study by Anderson (1974) found that the IEP of aluminum hydroxide, Al(OH)<sub>3</sub>, was 8.2 without any anion adsorption but shifted to 5.0 when the particles adsorbed a maximum amount of As(V). Protolyzable anions like As(V) shift this IEP value more than cations.



Figure 1. Representative shifts in electrophoretic mobility curves for adsorption of anions.
(a) Net charge at an adsorbent surface without anion adsorption.
(b) Net charge at an adsorbent surface with anion adsorption.
(c) Anion adsorption capacity as a function of pH. [Modified from Anderson (1974) and Stumm (1992)]

Figure 1 depicts this shift in terms of electrophoretic mobility (the velocity at which a particle travels under a given potential field). This parameter is relatively easy to measure for oxides, with positive mobilities corresponding to positively charged particles. Adsorption of anions increases the negative charge on the particle, thereby lowering the IEP and shifting these curves towards lower pH values. The amount of this shift increases as the concentration of the adsorbing anion increases until the maximum amount of As(V) is adsorbed. This corresponds to essentially monolayer coverage of the adsorbing anion on the adsorbent. Therefore, the IEP of the adsorbent depends on both pH and the concentration of anions in contact with the adsorbent.

Studies by Clifford and Lin (1985) and Hathaway and Rubel (1987) were performed with activated alumina for a target As(V) concentration of 50 ppb. These studies have shown that the arsenic adsorption capacity decreased significantly above pH  $5.5 \sim 6.0$ . This pH effect can be explained by surface charge theory. Even though the IEP of activated alumina is relatively high, pH 8.2, its IEP is shifted to lower pH upon the adsorption of arsenic or other protolyzable anions (See Figure 1). Thus, arsenic adsorption will significantly decrease the IEP to values around pH  $5.5 \sim 6.0$  depending on the amount of arsenic adsorbed.

We also tested a magnesium aluminate spinel (MgAl<sub>2</sub>O<sub>4</sub>) for its effectiveness in removing arsenic. This spinel is one of the hardest minerals in nature (hardness of 8.0). Recently, spinel has been extensively studied as an ultrafiltration membrane (Pflanz 1992) with high chemical stability. The spinel was synthesized using the method developed by Pan et al. (2001). We observed that the arsenic adsorption capacities for both spinel and gamma aluminum oxide significantly decreased when the pH of the source water was higher than the IEP of these adsorbents. However, surface charge measurements indicate that the IEP of spinel is some 2 pH units higher than the IEP of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Because of its higher IEP, the arsenic adsorption capacity of spinel was more than 2.5 times higher than that of activated alumina at pH 7.0.

Removal of As(III) from drinking water by adsorption (or ion exchange) is even more problematic than removal of As(V) because As(III) is uncharged over the pH range of 6.0 to 9.0, typical of drinking water (Clifford and Zhang 1994). 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 (Hering et al. 1996; Holm 2002). For similar reasons, ion exchange (Wang et al. 2000) and conventional coagulation filtration processes (Chen 1996) were also found to be ineffective in removing As(III).

Since groundwater is often present under anoxic conditions, the ratio of As(III) to As(V) is generally higher in groundwater than in surface water sources. As(III) also dominates when strong reducing agents are present (Smedley and Kinniburgh 2001). In Bangladesh, where arsenic problems have been severe, As(III)/As(V) ratios vary between  $0.1 \sim 0.9$ . In Mongolia, this ratio is  $0.7 \sim 0.9$  (Smedley and Kinniburgh 2001). In the US, only limited studies have been performed to determine this ratio. Recently, Aldstadt et al. (2002) reported a value near unity (As(III)/As(V)  $\approx 1.0$ ) 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) (Ghyrie and Clifford 2001). Previous research found that chemical oxidants including chlorine, ozone, and permanganate were effective in converting As(III) to As(V) (Frank and Clifford 1986; Amy 2000; Ghyrie and Clifford 2001).

During our studies, a new photooxidation-adsorption process has been investigated. This process combines oxidization and adsorption in a single step. Using sol-gel technology, boehmite (AlOOH) particles and  $TiO_2$  nano-particles were mixed and coated on glass beads that were then illuminated with a UV light source. This system allows for photooxidation-adsorption to occur in one step. Since the photooxidation-adsorption process requires neither the adjustment of pH nor the addition of chemicals, this process is much safer and more cost efficient for smaller and medium sized water treatment plants. Test results have shown that both arsenic species can be removed in a photocatalytic adsorption process using this novel thin-film material.

### **Materials and Methods**

#### <u>Materials</u>

All chemicals were reagent grade or better. All solutions were prepared using ultra-pure water. All glassware was cleaned by soaking in 10% HCl and rinsing four times with deionized (DI) water. The arsenite stock solution (1 g As/L) was prepared by mixing sodium arsenite, NaAsO<sub>2</sub>, (Sigma, 0.1 N standard solution) and 0.01 M sodium nitrate, NaNO<sub>3</sub>, (Sigma, American Chemical Society [A.C.S.] primary standard) solutions. The arsenate stock solution (1 g As/L) was prepared from sodium arsenate, Na<sub>2</sub>AsO<sub>4</sub>, (Aldrich, A.C.S. primary standard) dissolved in 0.01 M sodium nitrate solution. A certified standard inductively coupled plasma (I.C.P.) solution, 1,000 mg As/L, (Spex Certi Prep. Inc.) was used for calibration samples. With this experimental setup, pH was adjusted using HNO<sub>3</sub> or NaOH with 0.01 M NaNO<sub>3</sub> background electrolyte. The pH was initially adjusted to the target pH and readjusted after 1 hr. The final pH was measured just before the arsenic analysis.

To synthesize aluminum monohydroxide nano-particles, 2-butanol (Aldrich, 99+ %) and aluminum tri-sec-butoxide(ATSB),  $[C_2H_5CH(CH_3)O]_3Al$ , (Aldrich, 97%) were used. To make spinel, magnesium nitrate hexahydrate, Mg(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (Aldrich, 99% A.C.S. grade) was added to the synthesized aluminum monohydroxide nano-particles. Titanium (IV) butoxide, Ti[O(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>]<sub>4</sub>, (Aldrich, 99%) was used to synthesize TiO<sub>2</sub> nano-particles.

The particle size was measured by a Malvern Zeta Sizer 3000. This device includes a fixed quasi-elastic light scattering system (90° fixed). A standard silica nano-particle suspension (20 nm) was injected prior to size measurement and a  $\pm 10\%$  error margin was accepted. This instrument was also used to measure zeta potential as an estimate of the surface charge on the particles. Latex particle standards with an accepted zeta potential of -50 mV were injected before zeta potential testing and a  $\pm 10\%$  error margin was accepted.

The surface area of materials was measured as described by Drake (1995) with a Micromeritics ASAP 2010 micropore analyzer using the three-point BET method of  $N_2$  gas adsorption at liquid  $N_2$  temperature.

Boehmite (AlOOH) nano-particles were synthesized by sol-gel technology as described by Gieselmann (1991). The final concentration of solids in the boehmite sol was 35 g/L using a  $HNO_3$  to ATSB molar ratio of 0.07 for synthesis of the particles. Measurement by the Zeta Sizer 3000 indicated an average particle size of 20 nm at pH 4.0.

Calcining the boehmite at 350 °C converts it to gamma aluminum oxide,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The surface area of the synthesized aluminum oxide was 320 m<sup>2</sup>/g. This surface area is similar to that of the activated alumina currently used in water treatment.

Spinel particles were synthesized by sol-gel technology developed by Pan et al. (2001). These nano-particles have a core and shell morphology with spinel,  $MgAl_2O_4$ , as the shell and  $Al_2O_3$  as the core. In this method, the boehmite surface was modified to  $MgAl_2O_4$  by calcining at 550 °C with  $Mg(NO_3)_2$  while the core of the particle remained as  $Al_2O_3$ . During the firing process, magnesium oxide diffused toward the core and reacted with alumina, forming a spinel layer outside of the  $Al_2O_3$  particle (Pan et al. 2001). The surface area of the spinel gel was 220 m<sup>2</sup>/g.

Titanium (IV) butoxide, Ti $[O(CH_2)_3CH_3]_4$ , (Aldrich, 99%) was used to synthesized TiO<sub>2</sub> nanoparticles. When titanium butoxide is added to water, precipitation occurs immediately. The precipitates were stirred continuously until peptized. This peptized solution was dialyzed to clean the titania sol. The pH of the final sol was 3.5.

Prepared sols including boehmite, spinel, and titania were coated onto glass beads using a dip coating process. The coated media was calcined at temperatures between  $350 \sim 500$  °C.

#### Test 1: Batch tests to compare aluminum oxide and magnesium aluminate spinel

A series of batch tests were conducted using synthesized thin film coated media. The purpose of these tests was to establish and compare the kinetics for adsorption of arsenic at different pH values for the aluminum oxide and spinel. During this test, oxidation status was not considered and only As(V) was tested. The pH of the tested samples was varied between  $3.5 \sim 9.5$ . The initial arsenic concentration was 1,100 ppb and final concentration was  $650 \sim 1,040$  ppb depending on the pH of the solution.

### Test 2: Batch tests for mixed titanium oxide – alumina coated media

The purpose of this test was to study the As(III) removal kinetics using mixed alumina-titanium oxide-coated media. The experiments were performed in a UV lamp box. The initial concentration of As(III) was 3 ppm with 0.01 N NaNO<sub>3</sub> as a background electrolyte. Maximum UV irradiation time for this test was 24 hrs to simulate maximum oxidation efficiency. Studies of the oxidation kinetics of As(III) were conducted as well with the pH fixed at  $7.0 \pm 0.2$ . Similar blank experiments were performed to study the adsorption of As(III) by the mixed alumina-titanium oxide in the absence of UV light. To estimate the adsorption capacity of the mixed alumina-titanium oxide-coated media for charged arsenic, As(V), another adsorption test for As(V) without UV light was conducted.

Total arsenic concentrations were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Perkin Elmer Optima 4300 ICP-AES). Because EPA believes that the detection limit of ICP-AES for arsenic is 8 ppb (EPA 2000b), the final concentrations of arsenic for each batch test were controlled above 10 ppb.

#### **Results and Discussion**

#### **Tests of Adsorption Capacities**

The maximum adsorption capacity of the spinel was found to be 160  $\mu$ g As/m<sup>2</sup> (35.2 mg As/g spinel, 220 m<sup>2</sup>/g spinel) at pH 4.2 while the maximum adsorption capacity of the synthesized aluminum oxide was 105  $\mu$ g As/m<sup>2</sup> (33.6 mg As/g Al, 320 m<sup>2</sup>/g Al) at pH 3.8. Based on the surface area, the spinel has 50% higher adsorption capacity at low pH values (less than 5). However, the adsorption capacity of aluminum oxide and spinel were similar on a weight basis at low pH values.

As Figure 2 and Figure 4 illustrate, the measured IEP of the pure spinel was 10.2 while the IEP of pure aluminum oxide was 7.9 (i.e., the IEP of spinel was more than 2 pH units higher than aluminum oxide). After adsorbing arsenate on both materials, the IEP of the spinel shifted to 6.7, which is 1.4 pH units higher than that of aluminum oxide with monolayer coverage of arsenate and within the range of most water treatment plants. As shown in Figures 3 and 5, the adsorption capacity for arsenate for both materials decreases significantly, as expected, at pH values higher than the IEP because both the surface of the adsorbent and the arsenate adsorbate are negatively charged. Also note that, at slightly lower pH (less than 5), the arsenic adsorption capacity of the spinel was approximately 50% higher than the aluminum oxide. In this low pH range, in theory, both adsorbents should have similar adsorption capacity since this pH is far lower than the IEP of either adsorbent. The higher arsenic adsorption on spinel at these low pH values is likely caused by a difference in the number of adsorption sites on the surfaces of these materials. Based on geometrical considerations and chemical measurements, typical surface site

densities for oxides are 5 sites per square nanometer and range from  $2 \sim 12$  (Stumm 1992). Therefore, the higher capacity of spinel may be due to geometrical or surface chemical differences over aluminum oxide.

In the original IEP and adsorption studies of Anderson (1974), the adsorption capacity of alumina for anions significantly decreased at pH values above the IEP. This effect occurs because the surface of alumina covered with As(V) is no longer positively charged above pH 5.3 (see Figure 2). Therefore, this surface may not readily adsorb anions such as As(V) above this pH value. As the adsorbent loses positive charge, the electrostatic driving force for adsorption decreases. This explains the decrease in maximum capacity near the IEP.

As summarized in Table I, the slope of the adsorption curve increased  $5 \sim 10$  times as the pH was increased above the IEP (see Figures 3 and 5). This result indicates that the IEP of the adsorbent significantly influences the effect of pH on the adsorption capacity (i.e., adsorption of anions is essentially complete at pH values less than the IEP).

	below IEP		above IEP	
	Slope	r <sup>2</sup>	Slope	r <sup>2</sup>
Aluminum oxide	-3.05	1.0	-45.4	0.98
Spinel	-7.47	0.88	-46.7	0.95

**Table I.** Slope of simple regression line for adsorption capacity changes.

As Figures 6 and 7 illustrate, there is considerably more adsorption of arsenic on spinel  $(MgAl_2O_4)$  than on alumina  $(Al_2O_3)$  at pH 7 due to the higher IEP of the spinel. The increased adsorption capacity of spinel is maintained over a fairly wide pH range  $(5.5 \sim 9)$ . At pH 7, the adsorption capacity of spinel was 28.7 mg As/g spinel whereas the adsorption capacity of aluminum oxide was only 9.4 mg As/g alumina.

Figure 6 is constructed based on the results shown for adsorption data in Figures 3 and 5. Since the spinel has a higher adsorption capacity, adsorption site densities were normalized on a percentage basis in order to compare spinel against commercially available alumina. It was assumed that the maximum arsenic adsorption capacity occurs around pH 4.0 for both adsorbents. The utilized adsorption sites have been plotted over the pH range from 4.0 to 9.5. Utilized adsorption sites were calculated using the following equation:

Utilized Adsorption Sites(%) = 
$$\frac{\text{Arsenic Adsorption at Selected pH value}}{\text{Arsenic Adsorption at pH 4}} \times 100$$
 (eq 2.1.)



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**Figure 2.** Zeta potential curve for gammaaluminum oxide  $(\gamma$ -Al<sub>2</sub>O<sub>3</sub>)



Figure 4. Surface charge of spinel (MgAl<sub>2</sub>O<sub>4</sub>)



**Figure 6.** Adsorption capacity as a function of pH based on percent of sorption site utilization



**Figure 3.** Arsenic adsorption capacity for gamma-aluminum oxide( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) with 1,100 ppb of initial As(V)



**Figure 5.** Arsenic adsorption capacity of spinel with 1,100 ppb of initial As(V)



**Figure 7.** Adsorption capacity as a function of pH based on weight of adsorbent material

As already discussed, arsenic adsorption capacity significantly decreases above the IEP for both aluminum oxide and spinel. Since the spinel has a higher IEP than alumina, spinel can utilize more adsorption sites over the typical pH range  $(6.0 \sim 9.0)$  of water treatment plants. As Figure 6 illustrates, the spinel adsorbent utilizes 80% of its maximum adsorption capacity for arsenate removal at pH 7.0, whereas normal aluminum oxide only utilizes 30% of its adsorption sites at pH 7.0, a pH value typical of water treatment scenarios. Rosenblum and Clifford (1984) found that the maximum adsorption capacity of alumina was 25 mg/g at pH 6.0 and 4.5 mg/g at pH 8.0 when the equilibrium concentration (C<sub>E</sub>) of arsenate was about 500 ppb. Our test results were in agreement with this previous study (See Figure 7).

#### <u>Test of Single – Step Adsorption</u>

Oxidation status of arsenic in the source water significantly affects the adsorption capacity of adsorbents. Many arsenic removal processes were found to be ineffective for As(III), which is uncharged at the pH of drinking water. Therefore, it is difficult to remove As(III) by adsorption or ion exchange. For arsenite removal, As(III) is generally oxidized to As(V), which can be removed by adsorption or ion-exchange processes.

During our testing, a TiO<sub>2</sub>- Al<sub>2</sub>O<sub>3</sub> mixed oxide was developed and shown to effectively remove As(III) without requiring a separate oxidation process. A heterogeneous photocatalytic adsorbent (Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>) was synthesized by sol-gel technology. This adsorbent acts as a photocatalyst that oxidizes As(III) to As(V), after which As(V) is adsorbed on the catalytic adsorbent. This test utilized two types of nanoparticles, TiO<sub>2</sub> and AlOOH. These particles were mixed as a stable suspension (sol) that was used to coat glass beads. The effectiveness of the resulting thin-films after calcining at 350 °C was tested using solutions that contained 0.01 M NaNO<sub>3</sub> as a background electrolyte and initial concentrations of As(III) and As(V) of 3 mg/L. The pH of the solution was fixed at  $6.0 \pm 1$ . Adsorption was studied in the presence and absence of UV light. As shown in Figure 8, in the presence of UV light, the amount of As(III) adsorbed onto the mixed Al+Ti medium was almost identical to that of As(V). These results suggest that almost 100% of As(III) is oxidized to As(V) with this latter species being adsorbed by the film. Figure 9 shows that 70% of the As(III) is removed in two minutes.



**Figure 8.** Arsenic adsorption onto the mixed Al+Ti medium over a 24-hr period in the presence and absence of UV light.



Figure 9. Rate of adsorption of As(III) on the Al +Ti medium with and without UV light.

### **Conclusions and Recommendations**

This study confirmed that the IEP of the adsorbent was one of the most important factors for controlling the adsorption process in that the adsorption capacity for anions such as arsenate decreased when the pH of the source water was higher than the IEP of the adsorbent. Spinel media were shown to be more effective for arsenate removal at neutral pH than aluminum oxide media. At pH 6 – 9, the adsorption capacity of spinel media for removal of arsenate was more than 2.5 times higher than aluminum oxide. The difference in adsorption capacity between these two media was caused by their different IEP values (pH 7.9 for alumina and 10.2 for spinel).

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 indicated that photocatalytic adsorption may prove to be an effective single-step method for removing arsenite without requiring separate oxidation and adsorption processes. Arsenite was converted to arsenate and adsorbed onto the surface of the media within two minutes using TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mixed media.

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### APPENDIX A

#### Patents:

- 1. Simultaneous Removal of Arsenite As(III) and Arsenate As(V) From Drinking Water Using a Novel Photoactive Adsorbent (Disclosure P02323US).
- 2. Novel Adsorbent to Remove Protolyzable Anions from Water (Disclosure P02324 US).

#### Presentations:

- Eunkyu Lee, Marc Anderson, and Walter Zeltner Arsenic Removal Strategies Using Novel Adsorbent Material, 26th Annual Meeting, American Water Resources Association (AWRA)- Wisconsin Section (Oral Presentation) 3/7/2002.
- Marc Anderson, Isabel Tejedor, and Eunkyu Lee Photoactive Removal of As(III) from Water using Novel Al/Ti Active Material, 26th Annual Meeting, American Water Resources Association (AWRA)- Wisconsin Section (Oral Presentation) 3/7/2002.
- 3. E. Lee, M. Anderson, and W. Zeltner Arsenate and Arsenite Removal from Water Using Boehmite (AlOOH) Nano-particles, Midwest Groundwater Conference, Oral Presentation, 10/23/2001.