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Development of cerium dioxide coated alumina adsorbent to study the removal of arsenic from ground water

Laura Herder

DEVELOPMENT OF CERIUM DIOXIDE COATED ALUMINA ADSORBENT TO STUDY THE REMOVAL OF ARSENIC FROM GROUND WATER

Laura Herder

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Approved: _____
(Thesis Advisor)

_____
(Department Head)

Department of Chemistry
Rochester Institute of Technology
Rochester, NY 14623-5603

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Abstract

Arsenic contamination of groundwater is a major problem in both developing and developed countries as it is quite dangerous at extremely low concentrations and prevalent in many water supplies. Although there are many removal techniques for arsenic, the most promising for developing countries appears to be adsorption, since it is relatively low in cost, is easy to implement, requires no electricity, and can remove trace amounts of materials from solutions. Current adsorbents that have a high affinity for arsenic, but are costly because they have slow adsorption rates, low capacities, limited pH ranges, are affected adversely by competing ions, and often cannot be regenerated. One of the most successful adsorbent materials for arsenic removal is cerium dioxide, but unfortunately, this compound is quite expensive because of its rare earth component, cerium. Previous studies have utilized pure cerium dioxide adsorbents for adsorption. However, it is possible that some of the cerium dioxide may not be accessible to adsorption as a portion of this valuable chemical resides inside the particle itself.

This study examines the efficacy of a new adsorbent synthesized such that cerium dioxide nanoparticles are coated over an alumina substrate in an attempt to reduce cost and improve adsorption efficiency.   It is found that the coated alumina has fast adsorption rates (95% removed in 5 minutes), is effective over a large pH range, and also preferentially adsorbs arsenic even when other chemicals commonly found in groundwater, such as phosphates, are present. These results are comparable to those of pure cerium dioxide adsorbents and cerium dioxide coated carbon nanotubes used in previous studies. However, the adsorption capacity of the new adsorbent for arsenic is much lower than that for pure cerium dioxide nanoparticles. These results suggest that the effect of new environmental conditions on the efficacy of pure cerium dioxide as an adsorbent may be studied more cost effectively using the cerium dioxide coated alumina as a model system.

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CHAPTER 1

Introduction

1.1   Arsenic and its Challenges

Arsenic is a well-known poison to multi-cellular life, and its natural occurrence in drinking water remains a problem in many parts of the world. Arsenic derives its name from the Greek word arsenikon, meaning potent (Choong, 2007). Until recently, the symptoms of low doses of arsenic in humans were not easy to distinguish from other illnesses; at larger but still extremely low concentrations, arsenic causes death.

Arsenic is a metalloid and can exist in various allotropes. Arsenic is found in many minerals, mainly combined with sulfur or oxygen and with different metals, but it can also be found naturally in its elemental state. Arsenic ranks 20th in natural abundance on land, 14th in sea water, and 12th in the human body (Mohan, 2007). Although arsenic-containing minerals can be mined, most arsenic is released through natural processes such as weathering reactions, biological activity, geochemical reactions, volcanic emissions and other anthropogenic activities (Mohan, 2007). In addition to these natural causes, a growing amount of arsenic contamination is caused by mining and pesticide/herbicide by-products as well as combustion of fossil fuels. Both natural and man-induced processes thus lead to contaminated water and food supplies (Mohan, 2007).

Arsenic has often been used as a wood preservative because of its known toxicity to many organisms. However, the United States and the European Union banned this practice in 2004 as the toxicity of arsenic to humans and the environment became better known (Manda, 2002). Besides its wide use as a wood preservative, arsenic was also used for many other agricultural insecticides. Until the Poison-Free Poultry Act of 2009, arsenic containing compounds were used in industrial swine and poultry production as a method of disease prevention. There were many other uses for arsenic in a variety of fields, including art, military,

and pharmaceutical; however, these uses were on a smaller scale and have been phased out due to the increased knowledge of its toxicity.

Arsenic is actually needed as a micronutrient for the human body. It becomes carcinogenic when consumed in larger quantities, and accumulates in the body over a period of time (Peng, 2005). Since phosphorus and arsenic are both group 5A elements on the periodic table, they will form species that have similar chemical properties. Despite these similarities, there are important differences between arsenic and phosphorus containing chemicals as evidenced by their very different biochemical behavior (Antelo, 2005). Ingestion of inorganic arsenic can result in both cancer and non-cancer health effects. Arsenic interferes with a number of essential physiological activities including the action of enzymes, essential cations and transcriptional events in cells. The U.S. Environmental Protection Agency (EPA) has classified arsenic as a Class A human carcinogen. Chronic exposure to low arsenic levels (less than 0.05 mg/L) has been linked to health complications including cancer of the skin, kidney, lung and bladder, as well as other disease of the skin and neurological and cardiovascular system. The primary mode of exposure is ingestion of water containing arsenic. Dermal absorption of arsenic is minimal, and therefore hand washing and bathing in contaminated water does not pose a known risk to human health. In January 2001, the EPA published a final arsenic rule in the federal register. This rule established a revised maximum contaminant level for arsenic in drinking water at 0.01 mg/L, down from the World Health Organization's (WHO's) current limit of 0.05 mg/L (Kundu, 2006).

Arsenic contamination of groundwater is an important issue in many areas of the world. The largest populations at risk are in Bangladesh and West Bengal India (Mohan, 2007). It is estimated that 14.6 million people are exposed to drinking water containing arsenic with concentrations of 0.03 mg/L or higher (Zhang, 2003). Bangladesh and West Bengal have alleviated severe water shortages by providing drinking water at low cost to the rural populations through sinking of shallow tubewells in flood plain aquifers. Unfortunately, arsenic

contamination of shallow tubewell water in excess of acceptable limits has become a major public health problem in both of these countries (Ahmed, 2000).

Most of the contaminated ground water problems occur in developing countries since they have very limited access to other water sources. However, contamination is also a problem in developed countries. In the United States alone the annual cost for arsenic removal is 4.2 millions dollars (Vrijenhoek 2000). For example, in a 1987 ground water study conducted by the Wisconsin Department of Natural Resources, it was found that a large vein of arsenic-rich sulphide minerals in a bedrock layer had contaminated water supplies with arsenic levels of over 0.05 mg/L; over 20% of wells supplying water to more than 20,000 private customers were contaminated (Knobeloch, 2006).

1.2 Methods of Arsenic Removal

There are several current methods available to remove arsenic from water in large conventional treatment plants. However, because of electricity and operating costs, only a few of these methods can be used in developing countries. The most common of these methods include oxidation, co-precipitation and adsorption (Ahmed, 2000).

Oxidation is typically used in conjunction with other methods, since most treatment methods are effective in removing arsenic in its pentavalent form; therefore most methods include an oxidation step as a pretreatment to convert arsenite (trivalent form) to arsenate (pentavalent form). More detail about the forms arsenic forms can be found in Appendix C. Arsenite can be oxidized by many reagents, although atmospheric oxygen is most commonly used. This is because of its low cost and lack of chemical by-products after reaction. However the oxidation process is very slow, and it can take weeks to occur. Although oxidation is a helpful step in improving the efficiency of most arsenic removal processes, it does not by itself remove any of the arsenic from the ground water.

Although there are many references on technologies for removing arsenic, adsorption is becoming more attractive and promising because of its simplicity, sludge free operation, and regeneration capability (Kundu, 2006). Most other remediation methods are more effective at removing arsenic from water containing high initial arsenic concentrations (usually greater than 100 ppb or 0.1 mg/L) but these arsenic concentrations exceed the 0.05 mg/L water quality standard used in most countries (Mohan, 2007).

Several adsorptive media have been reported to remove arsenic form water. The efficiency of many of the adsorptive media depends on the oxidation step (described above). Saturation of media by different water contaminants takes place at different operation times depending on the specific sorption affinity of the medium to the given component (Ahmed, 2000). When materials other than arsenic adsorb, they consume active sites on the adsorbent that could be used for arsenic removal and thus compete with this process. Therefore, the selected media needs to preferentially adsorb arsenic compared with other components that may be present in the water. Traditional adsorbents for arsenic have slow kinetics, exhibit low adsorption capacities, and are hard to regenerate. Furthermore, although it is well known that fixed bed processes have higher adsorption capacities per unit mass of adsorbent than batch processes (Cussler, 2009), the slow kinetics dictates that batch adsorption processes are required. These factors increase the cost of arsenic removal.

1.3 Cerium Dioxide as an adsorbent

Activated alumina adsorbent is often used to remove phosphates, fluoride, and arsenic particularly in fixed bed reactors. However it does not adsorb contaminants well under certain conditions. Activated alumina operates well in a very narrow pH range of 5.5 to 7, but competing anions often limit its adsorption capacity, and the activated alumina is very hard to regenerate (Kundu, 2006). The adsorption process is also slow and limits the efficiency of fixed-bed adsorption. Besides activated alumina, some species of iron oxides have also been used as cheap

adsorbents; however these adsorbents exhibit similar problems of slow adsorption processes, low capacities and narrow pH ranges (Zhang 2005).

Deficiencies in existing adsorbent properties naturally lead to the consideration of alternative and novel adsorbents that have higher adsorption capacities, faster kinetics, and more favorable regeneration capabilities. It is desirable that these are accomplished at comparable or lower costs than existing adsorbents. Much current research focuses on use of rare earth metal oxides as adsorbents, since they have been shown to have high adsorption capacities for a variety of negatively charged species (Zhang 2005). Besides their high capacities, rare earth oxides have advantages of fast adsorption kinetics (Mohan, 2007). The most common rare earth element being studied is cerium as it is the most abundant of the rare earth metals and is thus the cheapest of this class of adsorbents. Still, it is more expensive than traditional adsorbents. A tradeoff, then, is whether any improvement in adsorption characteristics is outweighed by its increased cost. The current study attempts to assess the attributes of cerium-based adsorbents to provide a firm scientific framework for this decision.

It is known that cerium hydroxide exhibits a high selective adsorption for negative ions, such as arsenic, fluorine, and boron (Shimoto). Studies of ground water purification in northwest China show that fluoride does not compete with arsenic for binding sites in cerium hydroxide adsorbents, but phosphates do (Zhang 2003). It has been further suggested that a sacrificial ion can be used in a cerium oxide compound to allow for the adsorption of arsenic without an interference of phosphates since there is no commercial adsorbents specific for phosphates. Current studies show that calcium and magnesium, which are often found in drinking water, significantly enhance the adsorption capacity of arsenic on cerium dioxide coated carbon nanotubes in the presence of other competing ions (Peng, 2005).

Besides improving arsenic adsorption, mixtures of cerium oxide mixed with other metal oxides have been studied in order to compensate for the high price of pure cerium adsorbent. Although mixtures have been reported to slightly decrease the amount of surface area of the

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adsorbent and its adsorption capabilities (Zhang 2005), it has been outweighed by its benefits. Cerium oxides also have high regeneration capacities. In a 2005 study with arsenic, Peng (2005) showed that a strong base, NaOH, can remove the arsenic while keeping a high regeneration rate over 90%.

Another benefit of cerium oxides is that they possess the lowest solubility among the rare earth elements, meaning the adsorbent will not elute when the harmful ions in the water are being removed (Shimoto, 2007). As a result of all of the cited positive attributes of cerium oxides, a commercial cerium adsorbent has been put into practical use called READ-AS series by Nihonkaisu, Co, Ltd (Shimoto, 2007). Although this material works well as an arsenic adsorbent, previous literature has not determined optimal solution properties for arsenic removal with this material.

Since many journal articles report various conditions for optimum arsenic removal, the point of this study is to gather more information on cerium dioxide as an arsenic adsorbent. Previous methods used costly support material for the cerium dioxide (for example carbon nanotubes), whereas in this study the use of a commercially and cheap adsorbent is studied also in this study the use of smaller particles/larger surface areas to see the affect on adsorption.

1.4   The Current Study

Since many journal articles report various conditions for optimum arsenic removal, the purpose of this study is to examine the effect of ambient conditions on cerium dioxide as an arsenic adsorbent. Previous methods used costly support material for the cerium dioxide (for example carbon nanotubes), or pure cerium dioxide adsorbent particles. In the current work, cerium dioxide nanoparticles are coated on alumina to create a novel adsorbent in an attempt to study these effects using less cerium dioxide. Additionally, the potential of the new adsorbant material is assessed as a potential alternative to pure cerium dioxide particles. There are a

significant number of variables that potentially impact arsenic adsorption on cerium, and these

variables are studied systematically.

CHAPTER 2

Experimental Preparation of Adsorbent and Preliminary Studies to Maximize Adsorption Capacity

2.1 Preparation of Adsorbent

Literature cited in Section 1.3 indicates that cerium dioxide is effective at removing arsenic from ground water and shows promise as providing a reasonable compromise between efficacy and cost. In the current work, nanoparticles of cerium dioxide were utilized because smaller particles have larger surface area to volume ratios and thus more of the cerium dioxide is exposed for adsorption. Additionally, the efficacy of cerium dioxide nanoparticles in arsenic removal have not yet been studied. In order to limit the expense of the project and provide a potential alternative approach to effectively using cerium dioxide, cerium dioxide nanoparticles were grown on an alumina particle substrate. Although alumina has never been studied as a cerium dioxide support, alumina was chosen since it has been well studied as an adsorbent, can be manufactured in a reproducible way, and is inexpensive. The idea is to coat the alumina with cerium dioxide nanoparticles so that most of it is exposed and is available for adsorption. Commercially available cerium adsorbents are on the order of 25 microns in diameter. The nanoparticles of cerium dioxide used in this study are on the order of 1 micron in size, and therefore have a larger surface area to volume ratio which may improve the adsorption capacity per unit mass of cerium dioxide used.

Cerium dioxide coated adsorbent particles were prepared following the procedures described in the US Patent number 20100242342A1 and US Patent 20110056123A1. These patents describe the process for making pure suspended cerium dioxide nanoparticles. The method was altered in this work so that the nanoparticles were grown on alumina particles rather than being free in solution. The main chemical underpinning of this method is that cerium ions

(Ce^{3+} and Ce^{4+}) react with hydroxide ions to form cerium hydroxide. If the aqueous sample is heated; the cerium hydroxide converts into cerium dioxide. After these steps are completed, solutions containing the nanoparticles are placed in a muffle furnace to evaporate any remaining water solvent. The result is a dry cerium dioxide nanoparticle covering on the alumina. See Appendix B for experimental details on preparation of the coated particles. The result is a "standard" adsorbent that is used for further studies, summarized in section 2.8. Later chapters explore the effect of other components in the solution that affect adsorption of arsenic on this standard adsorbent.

2.2 Batch vs. Fixed Bed Column

The conditions under which the cerium dioxide coated alumina nanoparticles were produced could have an effect on the amount of arsenic adsorbed. To examine this possibility, it was necessary, very early in the study, to settle on an adsorption process technique so that comparisons between adsorbents produced under different controlled conditions could be made. Both batch and fixed bed absorption were assessed as possible processes. This section discusses some preliminary experimental results for the two methods, and justifies the choice of a batch process for adsorption for the experiments in this study. When considering the set-ups for both methods, the apparatus construction was important, as it was found arsenic may slightly bind to silicon dioxide, so no glass was allowed to come in contact with any arsenic sample. For both processes a 5 mL solution of an arsenic containing water sample was used (see Appendix B for more detail on arsenic sample preparation). To facilitate comparison between adsorption data from both methods, both methods used 325 mesh alumina with no coating available from Sigma Aldrich. Although the alumina has a low adsorption (at best only 22%), it was chosen as a reference since it was cheap; additionally since it was from the same manufacture lot, it would be more consistent than the cerium-coated alumina prepared in this study.

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The batch process was contained within a 20 mL plastic vial. A quantity of 0.50 grams of the dry adsorbent was put in a vial, and 5 mL of the arsenic containing water sample (see Appendix B for more detail on arsenic sample preparation) was added to the vial. The vials were capped and then consistently shaken for 1 hour on a VWR Vortex-Genie on setting 1, after which the samples were filtered before analyzing on the GF-AAS (see Appendix A for more detail on analysis of samples by GF-AAS). For fixed bed adsorption, an empty Solid Phase Extraction (SPE) column was used. The column was packed with 0.50 grams of the dry adsorbent. During passage of the 5mL arsenic water samples through the column, it was open to the atmosphere; no pressure or vacuum was applied to the SPE column.

For the batch process, the reproducibility error of the data showed a 28% variation. On the other hand the column method showed an average of 69% experimental variation in experimental reproducibility. It is not known why the column exhibited such inconsistent results, although it is hypothesized that a lack of consistent packing may have contributed. This hypothesis was supported by direct observation--when the packed material was removed some of the particles were still dry. Since the batch process was more reproducible than the column process, it was decided to run all of the experiments in this study using batch adsorption. Transient batch adsorption data provided in Section 4.1 revealed that equilibrium was typically reached before 1 hour of contact between the solution and the adsorbent. All batch adsorption data in this thesis is provided for 1 hour of time except for the time data in section 4.

2.3 Phosphate Levels

Previous studies have shown that phosphates and arsenic compete with one another during adsorption on solid surfaces (Antelo, 2005). Antelo has proposed that arsenic may interact with adsorbent surface groups more strongly because arsenic is larger in size than phosphate. Practically, most groundwater supplies have varying amounts of phosphates, and so its competitive adsorption with arsenic must be studied. Therefore, variation in phosphate levels in

solution was explored in all of the preliminary experiments used to determine the conditions under which the cerium-dioxide coated alumina particles should be made. Additionally, phosphate levels were also examined in all arsenic adsorption experiments reported in later chapters.

Aqueous solution concentrations of 0, 2500, 15000 and 25000 ppb (mg/L) of phosphates (made with sodium phosphates) were chosen, since phosphates concentrations in water are relatively high compared to the concentrations of arsenic (in this study 250 ppb). Except where noted, the following experimental conditions were used in all experiments presented in this and later chapters. A 250 ppb arsenic solution level was used, and solutions were created having a neutral pH to match typical groundwater conditions. A buffer was added to the arsenic samples since the addition of phosphates or arsenic to neutral water would shift the solution pH (for more detail about species of arsenic and phosphates in water see Appendix B). The buffer that was chosen was 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid, otherwise known as a HEPEs buffer. This buffer is commonly used in biology, specifically cell cultures. It was a good choice for the current study as it was readily available and known to work as a buffer with phosphates (phosphates are often present in biological reactions). Each arsenic-containing sample was prepared so that it contained a 0.015M solution of the HEPEs buffer. When this concentration was used, no pH changes were noted for the phosphate and arsenic levels described above as analyzed on the GF-AAS (see appendix A for more detail on method).

2.4   Variations of Loading of Cerium on the Alumina Particles

With the batch process identified as the standard technique to compare the adsorption capabilities of the cerium dioxide coated alumina, and the sensitivity of adsorption to phosphates being examined as in section 2.3, the effect of conditions under which the adsorbent was produced on its adsorption capability is now examined. As shown in the calculations in section Appendix D, 1.16×10^{-4} grams of cerium dioxide would be needed for every gram of alumina to

assure complete coverage of a spherical alumina surface. This calculation was based on a number of assumptions, the largest of which was that the alumina was spherical in shape and was smooth (contained no cracks/crevices). Since experiments to determine the exact surface area of the alumina have not been performed, 8 times the theoretical amount (base on the spherical shape) were added to make-up for possible errors caused by this assumption.

An experiment was performed to vary the amount of excess cerium dioxide during the creation of the adsorbent, and to assess its effect on adsorption. For the following experiment, adsorbents were prepared according to Section 2.8 and analyzed using the method discussed in Appendix A. One adsorbent was prepared with the standard of 8 times the theoretical amount and another sample was prepared with 16 times the theoretical amount. All other experimental procedures were the same, and the results are shown below.
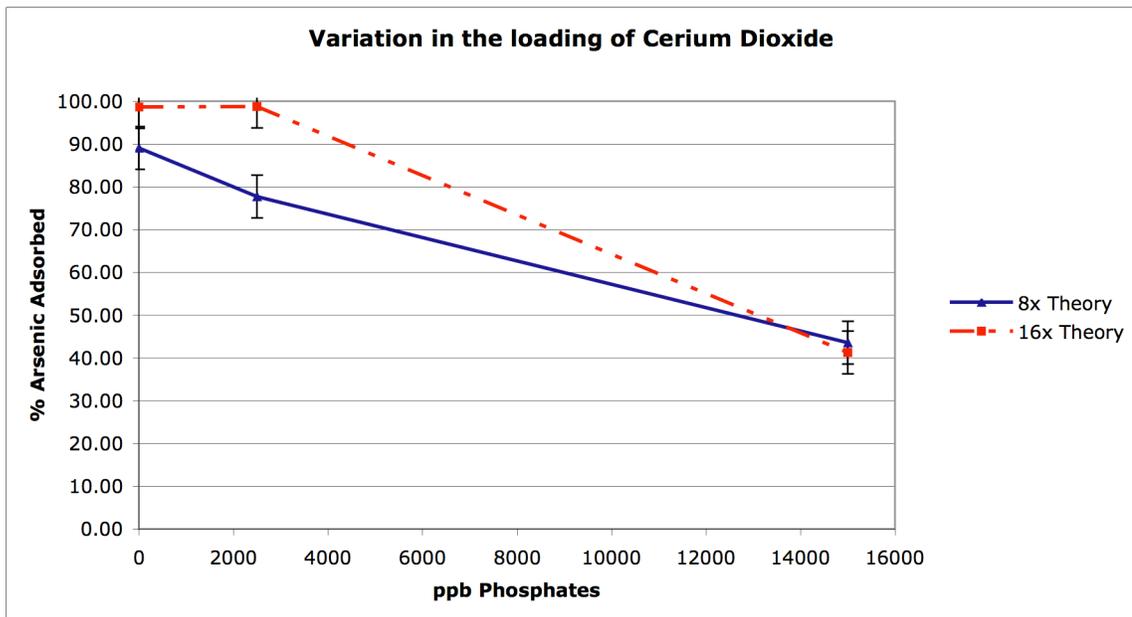
Figure 2.4-1: Percent Arsenic Removed vs ppb Phosphates, with a variation in amount of cerium dioxide loaded onto the alumina. Two different concentrations of cerium dioxide were grown on the alumina support, approximately $8x10^{-4}$ (8x Theory) grams cerium dioxide per gram of alumina, and $1.6x10^{-3}$ (16x Theory) grams cerium dioxide per gram of alumina .

Figure 2.4-1 shows that the adsorbent prepared with 16x the theoretical amount yields almost a 100% adsorption of the arsenic in the sample at low phosphate concentrations. This result suggests that more cerium dioxide is in fact resident on the alumina than the 8x theoretical

amount and suggests that the assumption of a smooth spherical shape is incorrect. Despite the improved performance of the 16x cerium dioxide adsorbent, the adsorbent is still very sensitive to phosphate concentration and the 8x and 16x adsorbents ultimately performs the same at higher phosphate levels. For all experiments in this thesis, the 8x theoretical amount was chosen as a standard unless otherwise noted.

2.5 Selection of Alumina Support Size to be Coated with the Cerium Dioxide Nanoparticles

In order to determine if the cerium dioxide particles were truly coating the alumina particles, two different mesh sizes (different diameter particles) of alumina were used. If the cerium dioxide particles were not coated on to the alumina particles, but the adsorbent was rather a mixture of alumina and cerium dioxide nanoparticles, changing the surface area of the alumina would show no impact on the amount of arsenic adsorbed. Alternatively, if there were significant differences in the adsorption, it would show that the cerium dioxide nanoparticles are in fact coated on the alumina particles.

Although the 100 mesh (0.15mm) alumina is larger in size than the 325 mesh (0.044mm) alumina, both were contacted with solutions of cerium dioxide nanoparticles so that the amount of cerium dioxide per gram of alumina (based on theoretical calculations of Appendix D) were the same. The two samples were otherwise prepared identically in accordance with section 2.8, and analyzed by the method described in Appendix A.
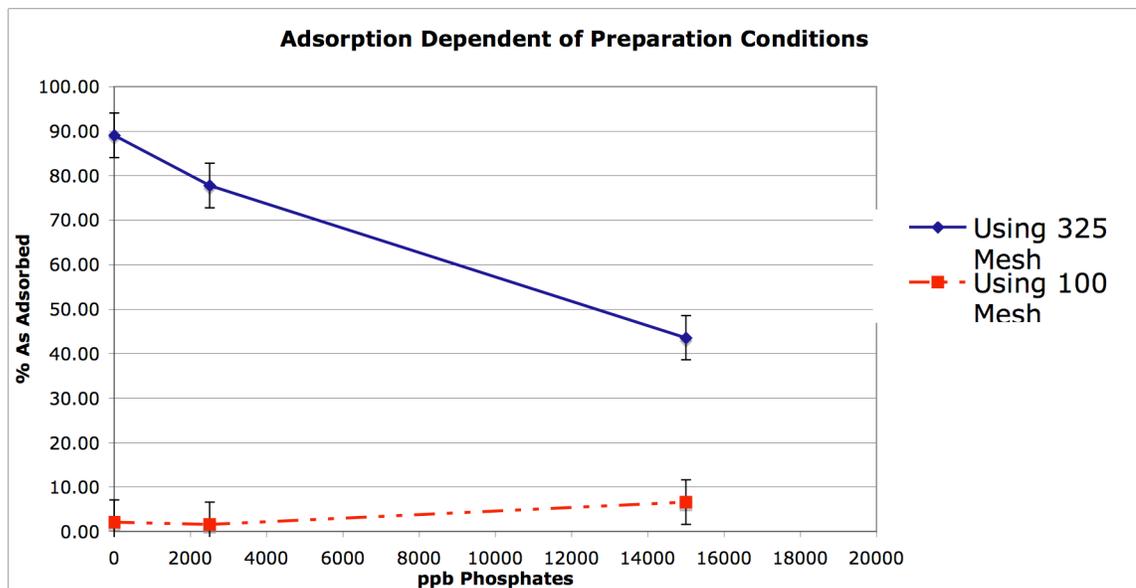
Figure 2.5-1: Percent of arsenic removed vs ppb Phosphates (mg/L) dependent on size of the alumina particles used when making the cerium-coated nanoparticles. Cerium dioxide was grown using the same method on 325 Mesh Alumina (0.044mm) and 100 Mesh Alumina (0.15mm).

Figure 2.5-1 shows that the 325 mesh and 100 mesh alumina had very different adsorption characteristics. The result indicates that size of the original alumina particle affects the amount of arsenic that can be removed from solution. This result allows us to deduce circumstantially that the cerium-dioxide nanoparticles are actually coated onto the alumina. If it is presumed that the only difference between the two alumina particles is the size and not their internal structure (the porosity is the same, for example), this result further suggests that arsenic adsorption is dependent upon surface area of the coated particle, an expected result consistent with standard adsorption theory (Cussler, 2009).

2.6 Effect of pH on the preparation of cerium dioxide coated alumina

As detailed in Appendix B, the cerium coated alumina particles can be created either in a basic (pH of 8.5) or acidic (pH of 4.5) solution. Both preparation techniques were studied to see if they impacted the ability of the arsenic to adsorb on the coated alumina particles. As described in section 2.8, experiments were performed using a batch process system and analyzed using the method described in Appendix A.

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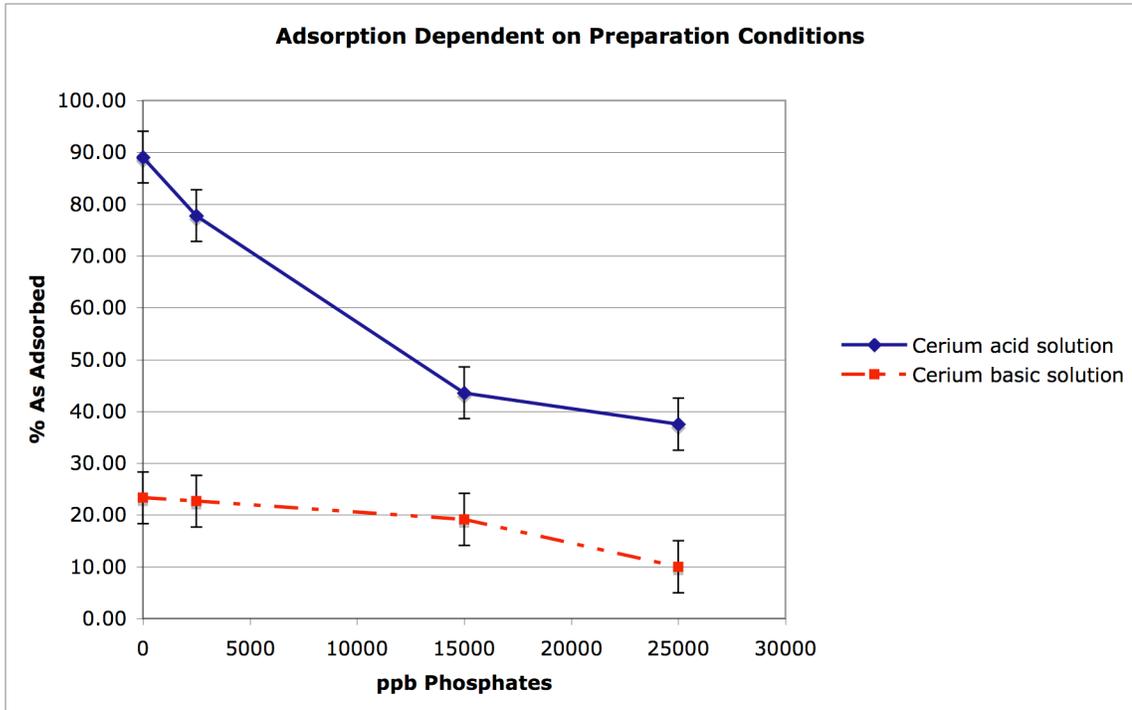
Figure 2.6-1: Percent of arsenic removed vs ppb Phosphate (mg/L) dependent on preparation pH used when making the cerium-coated nanoparticles. For the Cerium acid solution, cerium dioxide coated alumina particles grown at a pH of 5, and for the Cerium basic solution, the cerium dioxide coated alumna particles were grown at a pH of 10.

As shown in figure 2.6-1, adsorbents prepared in different pH solutions were negatively affected by a higher concentration of phosphates. However results show that the cerium particles created in the more acidic conditions did have a higher arsenic adsorption than the particles created in the basic conditions. These results were consistent for all studies performed and as a result, all coated alumina particles were prepared in acidic solutions.

2.7 Effects of Calcining temperature on the preparation of cerium dioxide coated alumina

As described in section 2.8, once the cerium dioxide was grown or coated on the alumina particles, the particles in their aqueous solutions were placed into a muffle furnace. The calcining temperature used during the creation of the adsorbent was studied to see if it had an effect on

arsenic adsorption. Two temperatures were examined: 400 C and 700 C. After calcining, the

method used was of that described in section 2.8, and analyzed using the method described in

Appendix A.

<figure>
Adsorption Dependent of Preparation Conditions

Y-axis: % As Adsorbed (0.00 to 100.00)
X-axis: ppb Phosphates (0 to 30000)

Legend:
— Calcined at 400
— ▲ — Calcined at 700
</figure>
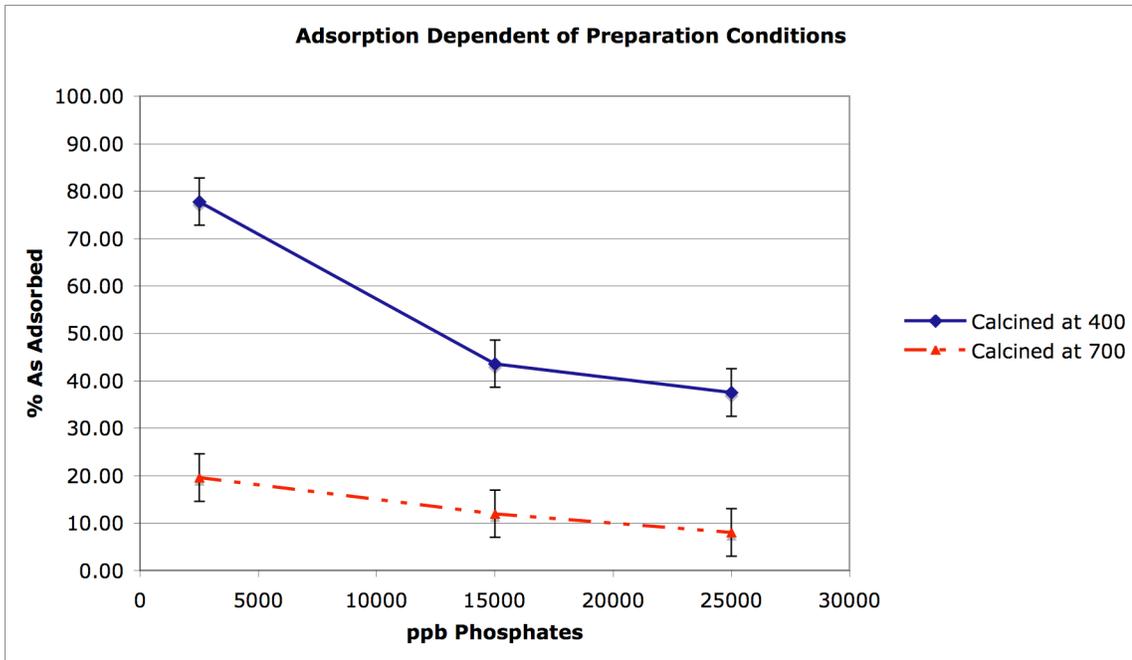
Figure 2.7-1: Percent of arsenic removed vs ppb Phosphate (mg/L) for 400 C and 700 C calcining temperatures used in the preparation step. The two cerium dioxide coated nanoparticles were otherwise both prepared in the same manner, following the procedure in section 2.8.

As figure 2.7-1 indicates, higher calcining temperatures lower the percent of arsenic

adsorbed in the solution. It hypothesized that at temperatures of about 700 C the cerium dioxide

nanoparticles may be sintering, and this may decrease the surface area for arsenic adsorption,

resulting in lower adsorption. As a result of this experiment, future experiments were performed

with cerium dioxide coated alumina particles that had been calcined in a muffle furnace at 400 C.

Regardless of calcining temperature, Figure 2-5.1 shows that arsenic adsorption is favored at

lower phosphate concentrations.

2.8 Summary of Experimental Conditions

For all further experiments in this study, cerium-dioxide nano particles were coated on 325 mesh alumina from Sigma-Aldrich, in an acid solution (pH=4.5) and calcined at 400C. All further experiments were conducted using a batch process, using a 0.015M HEPEs buffer, with 250 ppb Arsenic with various concentrations of phosphates. All batch adsorption data in this thesis is provided for 1 hour of time except for the time data in section 4. For further detail on sample preparation see Appendix B. All arsenic samples were characterized using the method outlined in Appendix A.

CHAPTER 3

Effect of Water Conditions on Arsenic Adsorption

3.1 Introductory comments

In Chapter 2, the conditions under which the Cerium dioxide coated alumina was created were explored to assess its adsorption capacity. A standard adsorbent preparation was identified and summarized in section 2.8. The main scope of this present study is to find a cost-effective means of using cerium dioxide adsorbents for arsenic removal of ground water. The effect of water conditions on the standard adsorbent is now explored in this chapter.

3.2 Effect of pH on Arsenic Adsorption.

Groundwater typically has a neutral pH. However, there are commercial applications where the pH may not be neutral, such as in arsenic contaminated wastewaters, and so the effect of pH on arsenic removal must be studied. It is also desirable to examine the effect of pH on arsenic adsorption to gain insights into the adsorption mechanism itself. Previously studies have indicated that cerium dioxide adsorbents work effectively over large pH ranges, and it is necessary to see if this behavior is similar for the cerium dioxide coated alumina adsorbent used in this study.

In a first study, the effect of pH on the adsorption of arsenic on 325 mesh alumina (no cerium dioxide coating, 0.044mm) was examined. Three different arsenic solution pH values were studied-- a neutral pH of 7, a basic pH of 8.5, and an acidic pH of 5.2 using Hydrochloric acid or Sodium Hydroxide. The pH was changed in the arsenic sample before adding the sample to the adsorbent, and for these studies no HEPEs buffer was used. As these samples were not standard (all other solutions in this work used the buffer), separate standards were prepared and

analyzed on the GF-AAS (appendix A for more detail on method). No discernable absorbance differences were observed on the instrument regardless of whether the HEPEs buffer was used. Different phosphate concentrations were examined as discussed in section 2.3. Figure 3.1-1 indicates that alumina adsorbent performs best at a neutral pH at low phosphate concentrations, which was expected from previously cited studies (Mohan, 2007).
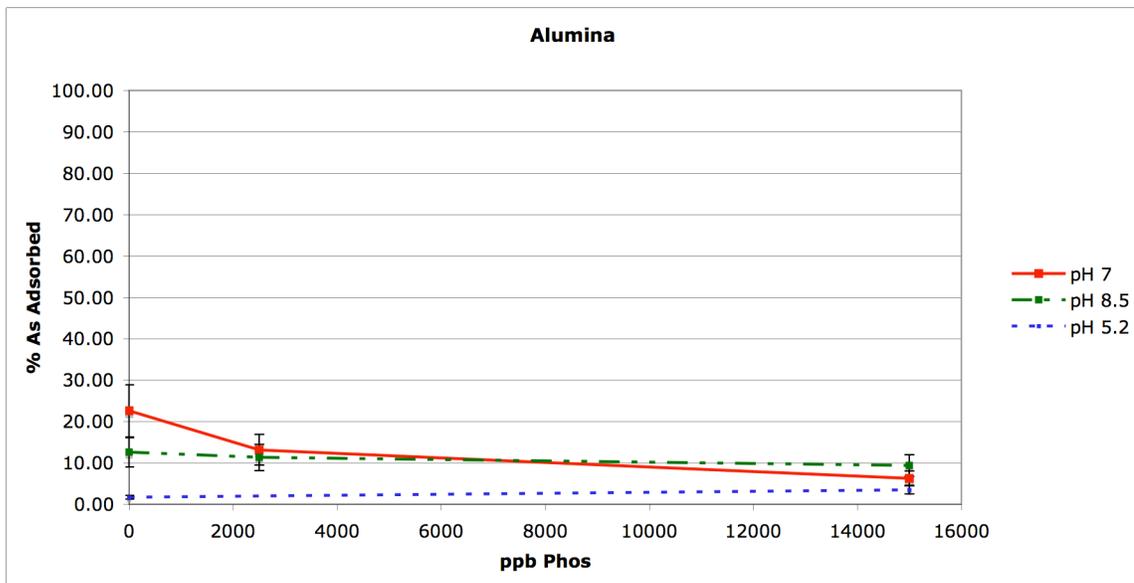
Figure 3.1-1: Percent arsenic adsorbed on 325 mesh Alumina (from Signma Aldrich) vs. the ppb Phosphates (mg/L) as a function of three different pH values (pH 5.2, pH 7 and pH 8.5)..

The next study was done using cerium dioxide coated alumina (see section 2.8 for adsorbent preparation). As in the alumina study described above, the various pH level arsenic solutions contained no HEPEs buffer, and the pH was changed before adding to the adsorbent. In this study 4 arsenic solutions were examined: neutral (pH 7), acidic (pH 5.2) and basic (pH of 8.5 and 10.6).
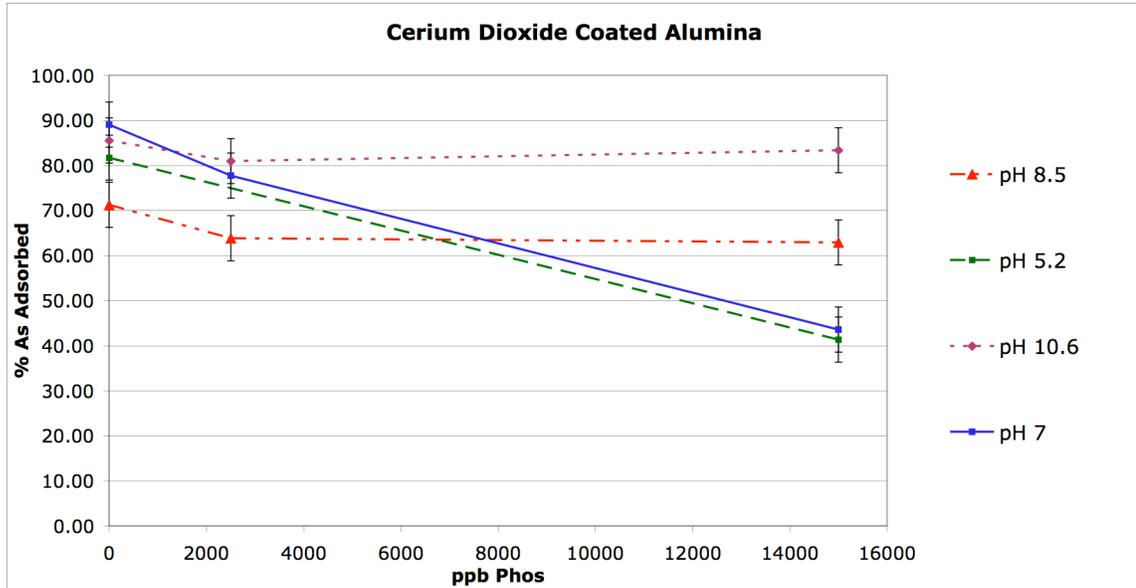
Figure 3.1-, Percent arsenic adsorbed vs ppb Phosphates (mg/L) added to the water sample using a cerium dioxide coated alumina adsorbent at various pH levels(pH 5.2, pH 7, pH 8.5 and pH 10.6).

Figure 3.1-2 indicates that arsenic adsorption on the cerium dioxide coated alumina particles is not strongly dependent on the pH of the sample at lower phosphate concentrations. However, at higher levels of phosphates, the solutions appear to be insensitive to phosphate amount and therefore may be advantageous. It is hypothesized that these results may arise because of the expected oxidation state transition (+3 to +4 state) for cerium at a pH of 8 or the various oxidation states of arsenic (see Appendix C). Although the sensitivity of pH might be useful in some applications, it was not further studied since the focus was on groundwater treatment application, which typically occurs at or near neutral pH. Nevertheless, the data trends may be used in future work to better understand the nature of the arsenic adsorption process.

3.3 Effect of Dissolved Oxygen on Arsenic Adsorption

It has been shown that the pH can have a significant effect on arsenic adsorption (Section 3.2) . It is hypothesized that this effect is invoked by the pH affecting the charge on the arsenic (can be both +3 or +5) and the cerium (can be either +3 or +4); see Appendix C for more details. Another means of adjusting these charges might be accomplished by changing the solution

environment to be either oxygen rich or oxygen poor. It has been proposed in other studies (see section 1.2) that an oxygen rich environment would favor the pentavalent arsenic in solutions which by other adsorption methods is easier to adsorb than the trivalent form. The following details experiments to examine this possibility.

A first experiment was performed on the cerium dioxide coated alumina using the a water sample that contained 250 ppb Arsenic with a 0.015M HEPEs buffer at neutral pH, compared with an identical sample that also had hydrogen peroxide added. Note that hydrogen peroxide was used since bubbling oxygen gas through the sample was a safety concern as it could lead to a fire hazard.
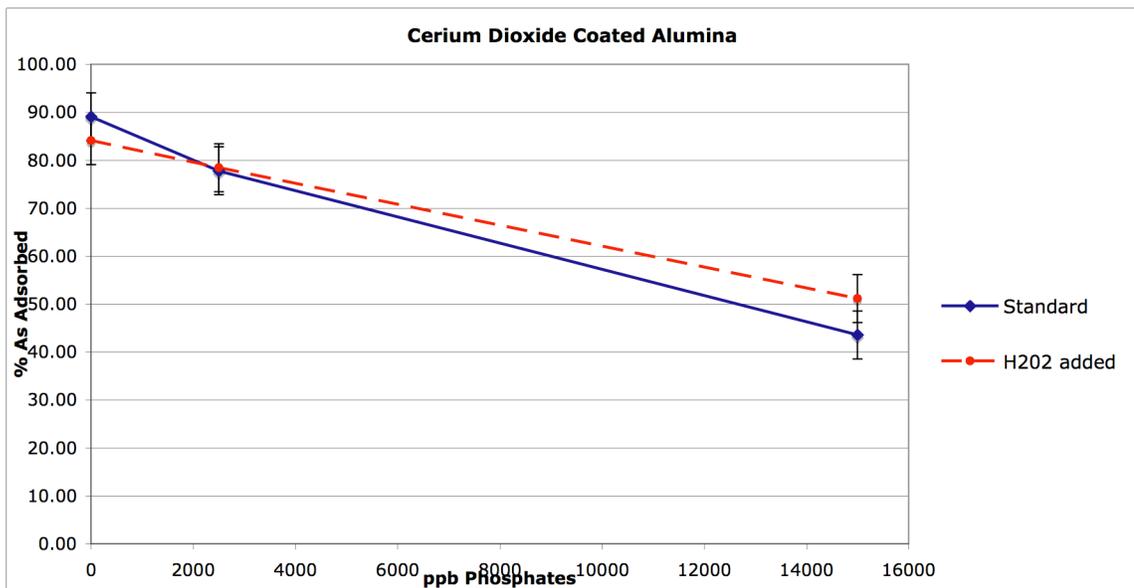
Figure 3.2-1, Percent arsenic removed vs ppb Phosphate concentration for cerium coated alumina in standard water sample and an oxygen rich water sample. Both samples were prepared with same amount of arsenic (250 ppb) and various phosphate concentrations. One sample was considered the standard (neutral pH, see section 2.8) and the other arsenic water sample was the same as the standard but with hydrogen peroxide added.

Figure 3.2-1 indicates that there is little difference in the adsorption capacity when the solution is oxygenated. It is hypothesized that the cerium dioxide coated alumina maybe be able to remove both arsenic 3 and 5 just as easily; alternatively, since the standard sample is open to air, it is also possible that the standard already contains a predominant amount of arsenic 5.

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Next the effect of an oxygen poor environment was examined. To serve as a control, a

stock solution containing the arsenic (prepared in accordance with Appendix B) was put in

contact with adsorbent and results were collected at various phosphate levels. Next, a portion of

the same stock solutions was exposed to nitrogen gas, which was bubbled through the water

sample for 1 hour prior to contacting the adsorbent. It was hypothesized that this creates an

oxygen-depleted environment, and so the arsenic would revert to its trivalent state, and in

accordance with cited studies (see section 1.2) might therefore be more difficult to adsorb.
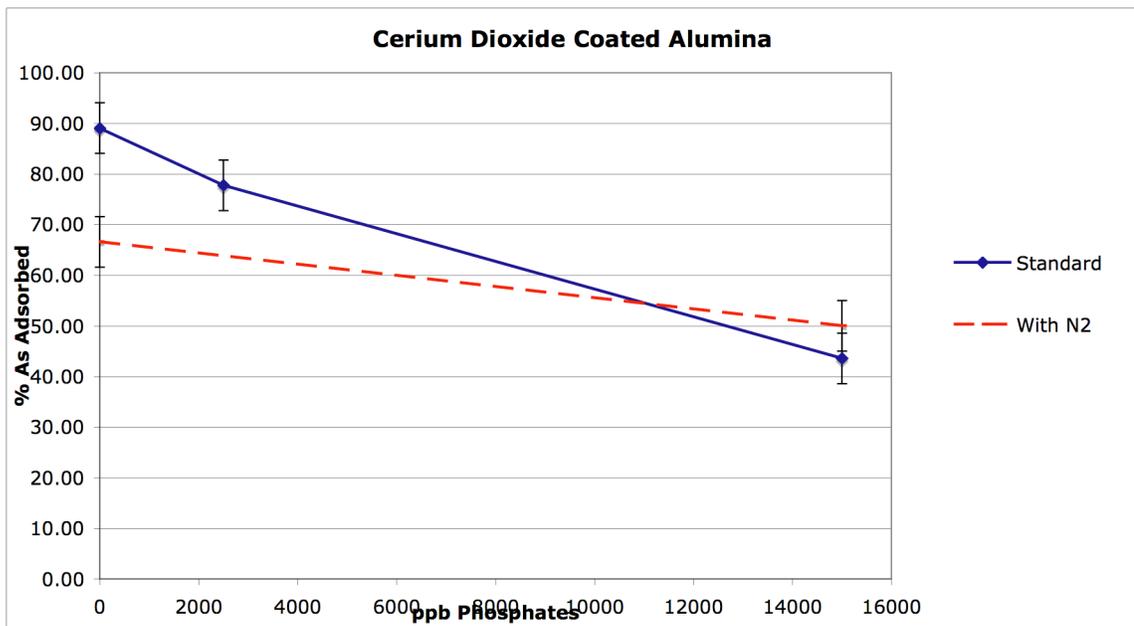
Figure 3.2-2, Percentage of arsenic adsorbed on cerium dioxide coated alumina vs. ppb
Phosphates, comparing a standard water sample to an oxygen poor water sample. Arsenic was
removed from a standard water sample (section 2.8) compared to an identical sample but with
Nitrogen bubbled through it for one hour prior to the adsorption.

Figure 3.2-2 provides results of the experiment. Although there is a decrease in the

arsenic adsorbed in an oxygen poor sample, there still is a much higher adsorption than

previously cited adsorbents (Mohan, 2007), which require a pretreatment step to oxidize the

environment. The data of figure 3.2-2 suggests that at low phosphate levels, pre-treating a

deoxygenated water sample (perhaps from a stagnant water source) may be beneficial in

enhancing adsorption. At higher phosphate levels, it appears that there is little benefit in pre-treatment of water samples.

3.3   Effect of Temperature on Arsenic Adsorption

It is well known that adsorption is highly dependent on temperature; many adsorbents have higher solute loadings as temperature increases. All previous experiments in this study were performed at room temperature (20C), so a preliminary experiment was performed to examine temperature dependence. This could be important, as developing countries where arsenic remediation is required often have relatively high ambient temperatures. Two temperatures were studied in this preliminary examination of adsorption of a standard arsenic solution on cerium dioxide coated alumina: 20C and 40C.
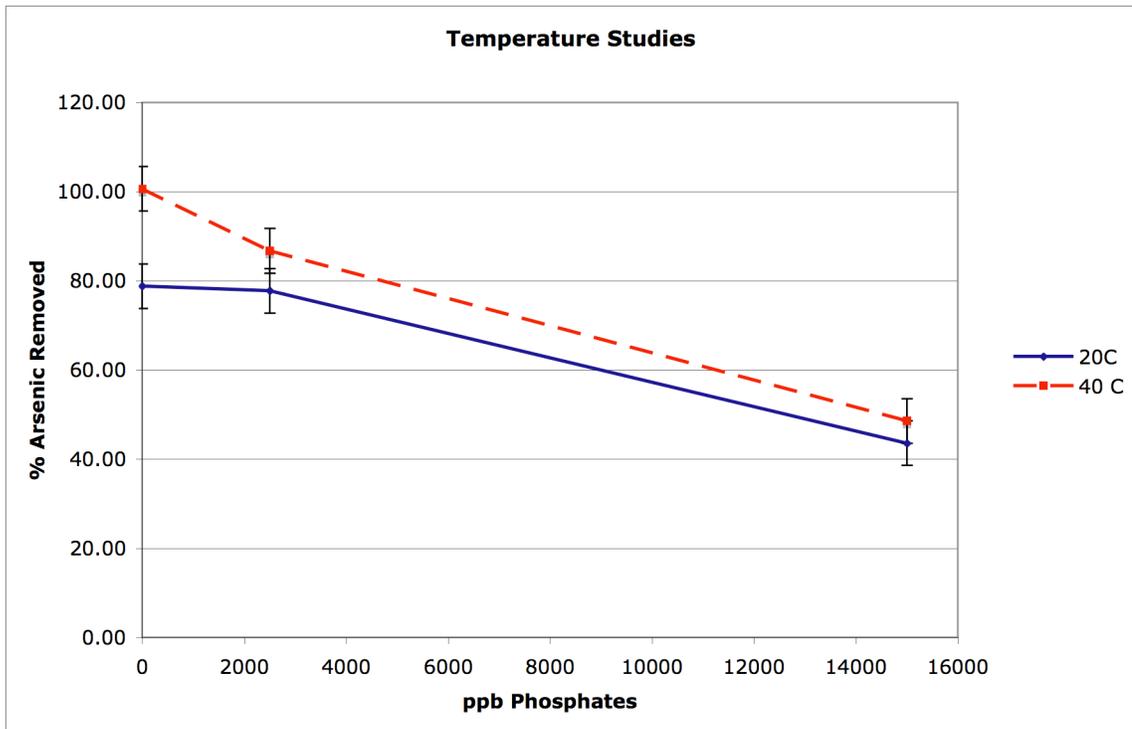
Figure 3.3-1, Percent arsenic removed vs. ppb Phosphates (mg/L) for two temperatures on cerium dioxide coated alumina adsorbent (Section 2.8).   Arsenic was adsorbed from a stock water sample (Appendix B) at two different temperatures, 20 and 40 degrees Celsius.

Figure 3.3-1 shows that the higher temperature yields increased adsorption for the lower phosphate concentrations, but only gives a slight increase in the adsorption for high phosphate

levels. More data will be required to examine the temperature dependence in more detail; however this preliminary study shows promising results for higher temperatures.

3.4 The Use of Other Metals to Enhance Adsorption

Cerium dioxide coated alumina may be mixed with other metals to reduce its cost and, potentially, to help reduce the detrimental influence of phosphates. In this section, experiments are presented to examine the relative adsorption capability of metals that are coated on alumina supports. This is in an attempt to identify particular candidates to create mixtures with the Cerium dioxide coated alumina adsorbent to enhance their performance. We now describe the method by which various metals were selected, as well as some data showing their performance.

In order to select appropriate metals, the value of the solubility product (K_{sp} or log of that value the pK_{sp}) for each metal with an arsenic species and a phosphate species were examined. A large number of K_{sp}'s are calculated and listed in many reference books. Although the value for cerium with a phosphate species is known ($CePO_4$ has a pK_{sp} of 23.0) there are no reliable K_{sp} values for cerium and an arsenic species. If the values were known, estimates could be made as to whether arsenic would bind better than the phosphates to the cerium at equilibrium. An additional consideration in the selection process was whether the metal had been examined in previous adsorption methods, cost, and availability in the lab.

The first metal to be studied was iron, chosen because of its availability, low cost, and its previous use as an adsorbent. Since iron's pK_{sp} values with arsenic and phosphate species are relatively close (20.2 for $FeAsO_4$ and 21.9 for $FePO_4$) it would be expected that iron will be affected by the amount of phosphates present in solution. The iron coated alumina was prepared in the same way as the cerium dioxide (see appendix B). Calculations were performed to determine the grams of iron necessary to obtain an 8x concentration of metal in solution following the procedure in Appendix D.

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Study of Iron as an Adsorbent
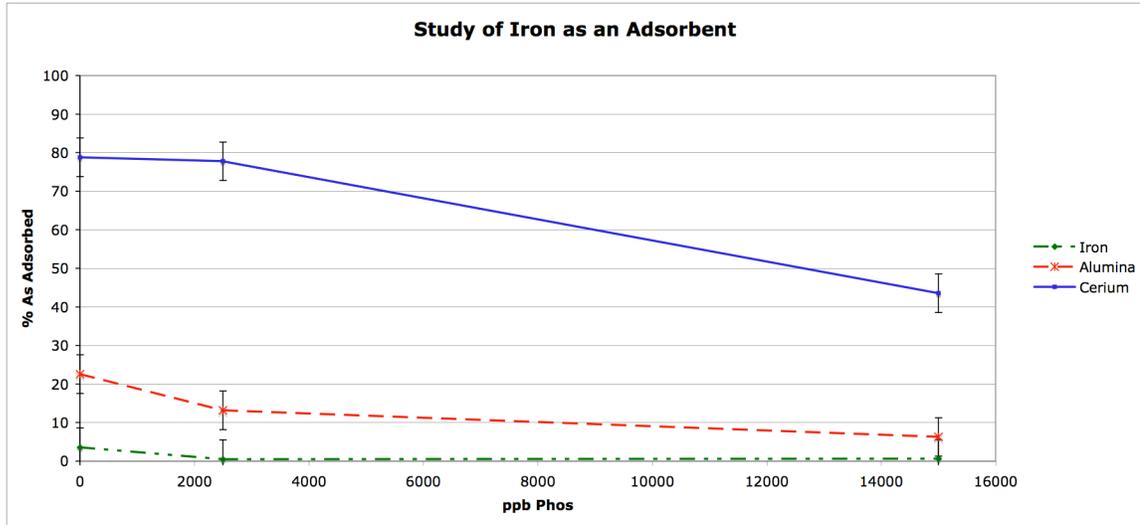
Figure 3.4-1: Percent arsenic adsorbed vs. ppb Phosphates (mg/L), comparing arsenic adsorption using various adsorbents: Alumina 325 mesh from Sigma Aldrich(purple), Alumina coated with Iron (blue), and Alumina coated with Cerium (pink).

Figure 3.4-1 provides results comparing the adsorption capacity of the iron coated alumina, pure alumina, and cerium dioxide coated alumina adsorbent. The data indicates that uncoated alumina performs better as an adsorbent than iron-coated alumina. Also the iron coated alumina exhibits no improvement in arsenic adsorption with higher levels of phosphates. As a result of this study, iron coated on alumina was ruled out as a choice for adsorbent to mix with the cerium-dioxide coated alumina.

The next metal to be considered was calcium. Calcium was chosen also because of its low cost and availability in the lab. Additionally, a previously cited study (Peng 2005) showed an increase in adsorption of arsenic when calcium is present when it is either free in solution or on the adsorbent. Once again, the calcium coated alumina was prepared in the same manner that the cerium coated alumina (appendix B). Although the pK_{sp} for calcium and arsenic species,$Ca_3(AsO_4)_2$, is 18.2 which is lower than the iron's, calcium's pKsp with a phosphate species, $Ca_3(PO_4)_2$, is 28.7. Since calcium will bind to phosphates more than it will to the arsenic, it is thought that the calcium can act as a sacrificial ion in the adsorbent to remove the phosphates so that they do not interfere with arsenic adsorption
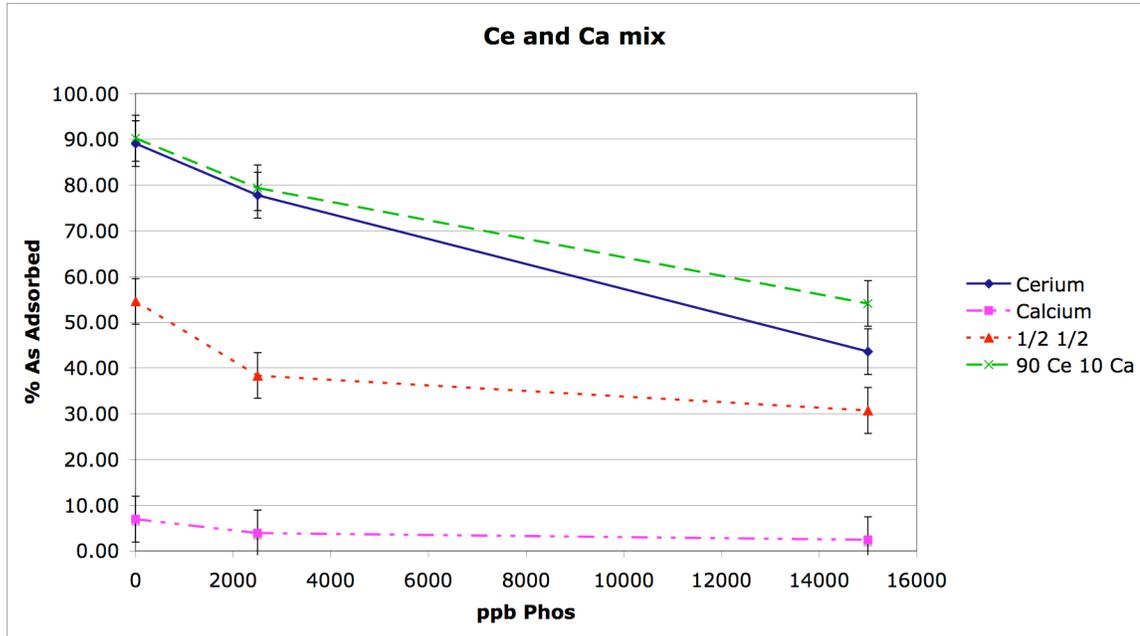
Figure 3.4-2: Percent of arsenic adsorbed from solution vs. ppb Phosphates in solution using various adsorbents: Cerium coated alumina (blue), calcium coated alumina (pink), a 1:1 mixture of the two (red) and a 9:1 mixture of Cerium to Calcium.

Figure 3.4-2 indicates that calcium-coated alumina shows little adsorption of arsenic, however it was further studied because of the results shown in Peng (2005). In this study it might be expected that a 50/50 mixture of the two different coated alumina's would yield adsorption results between those for cerium and calcium. This was indeed the case for the lower two concentrations of phosphates; at a higher level of phosphates however, the mixture exhibited adsorption closer to that of the 100% cerium. A mixture containing 90% cerium dioxide coated alumina and 10% calcium coated alumina was then tested. For the lower phosphate concentrations, the adsorption of arsenic is the same on the pure calcium and the 90/10 mixture, but at high phosphate concentrations of phosphates, the adsorption is better when the 90/10 mixture is used.

It can be concluded that if the water sample contains high levels of phosphates it may be beneficial to add calcium-coated alumina to the cerium-coated alumina. More cost analysis must be done to determine if it would be cheaper to use a mixture of calcium and cerium for lower concentrations of phosphates. Using the same theory applied to known values of K_{sp}, it would

appear that other metals such as Barium, Lithium and Cobalt may work as well as sacrificial ions; however examination of these possibilities was beyond the scope of this study.

CHAPTER 4

Transient Adsorption, Preliminary Isotherm, and Adsorbent Regeneration

4.1 Transients

As reported in a review by Mohan (2007), most studies for arsenic removal using rare earth metal oxides show that 90% of the adsorption takes place within the first 10 minutes. Although all of the batch studies (described in section 2.2) have a process time of 1 hour, a time study was required to compare the adsorption rate for cerium coated alumina particles to those of rare earth oxides described elsewhere. The time study was also required so that enough time was allotted so that all experiments in this work were assured to be at equilibrium.

Three time studies were completed; all contained 5 mL of the same arsenic solution with 250 ppb Arsenic, and 0.015M HEPEs buffer with no phosphates, and the batch process was performed in the same manner described in section 2.8. However instead of using the 1 hour mixing time, the mixing time was varied from 5 minutes to 90 minutes and measurements taken in regular intervals. Adsorbent types were varied with cerium dioxide coated alumina particles prepared using the standard preparation (8x the amount of cerium needed to completely coat a fictitious spherical alumina particle, see section 2.8), double the standard preparation (16x the amount of cerium needed to completely coat a fictitious spherical alumina particle; see section 2.7), and cerium dioxide nanoparticles from Sigma-Aldrich (25nm).
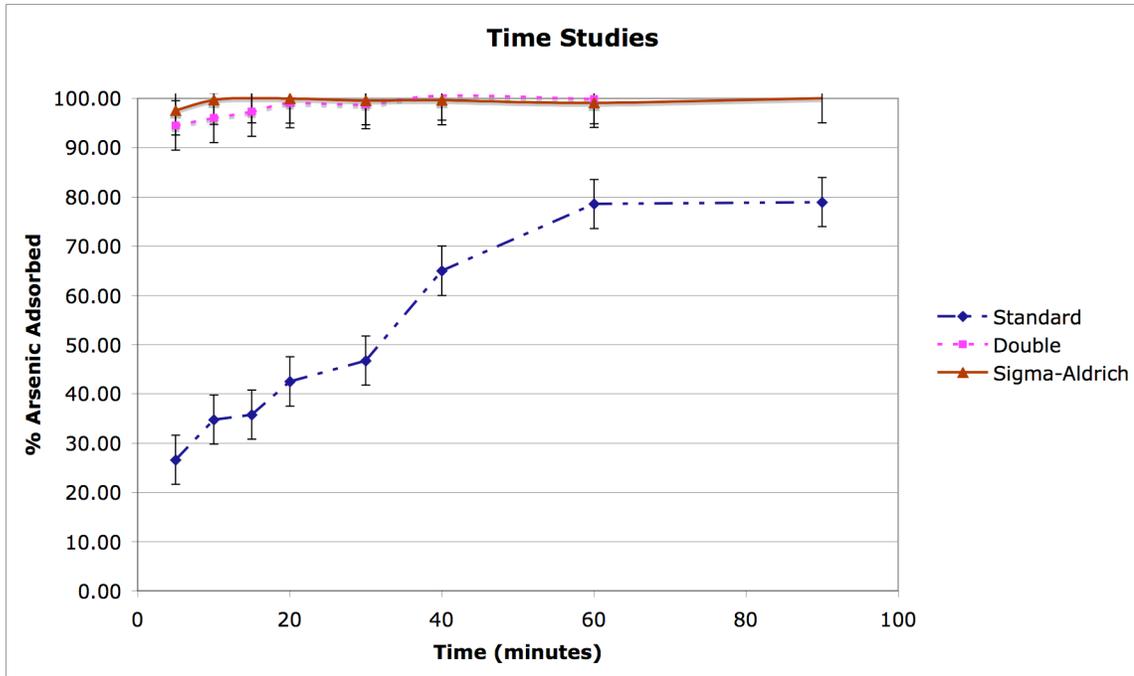
Figure 4.1-1Percent arsenic adsorbed vs time for three different arsenic adsorbent. Adsorbents used were the standard cerium coated alumina 8×10^{-4} grams cerium dioxide per gram of alumina (Appendix B), double the standard coated on alumina, and a 25nm cerium dioxide nanoparticle from Sigma Aldrich.

Figure 4.1-1 shows that the standard prepared cerium dioxide coated alumina particles take longer to adsorb than the double concentration prepared cerium dioxide coated alumina. Additionally, the double concentration prepared adsorbent performs comparably to that of the Sigma-Aldrich cerium dioxide nanoparticles. The latter materials show that over 90% of the adsorption takes place within 5 minutes. Since all of the time series for the different adsorbents took place within an hour, it shows that an hour is a reasonable estimate for the time to wait until unit equilibrium adsorption is essentially obtained. An hour was subsequently used in all studies as the time at which equilibrium loading was assumed to occur. Additional time studies may need to be completed with various phosphate concentrations to see if phosphate levels affect the adsorption rate on arsenic, indicated by previously cited studies; however, phosphate is known to adsorb more quickly than that of the arsenic, so the assumption of 1 hour was assumed valid for the varies phosphate levels.

4.2 Preliminary Isotherm

In all previous experiments performed in this study, water solutions contained 250 ppb arsenic (250ug/L). This concentration was chosen to provide an optimum distribution in the calibration curve used for the GF-AAS (see Appendix A for more detail). To construct an isotherm necessary for applications, however the adsorption of various arsenic solution concentrations need to be studied. The adsorbent that was used was the cerium dioxide coated alumina and all other experimental procedures were the same as previously described in Appendix B, except that the water samples contained 150, 250, 350, and 500 ppb arsenic with no phosphates.
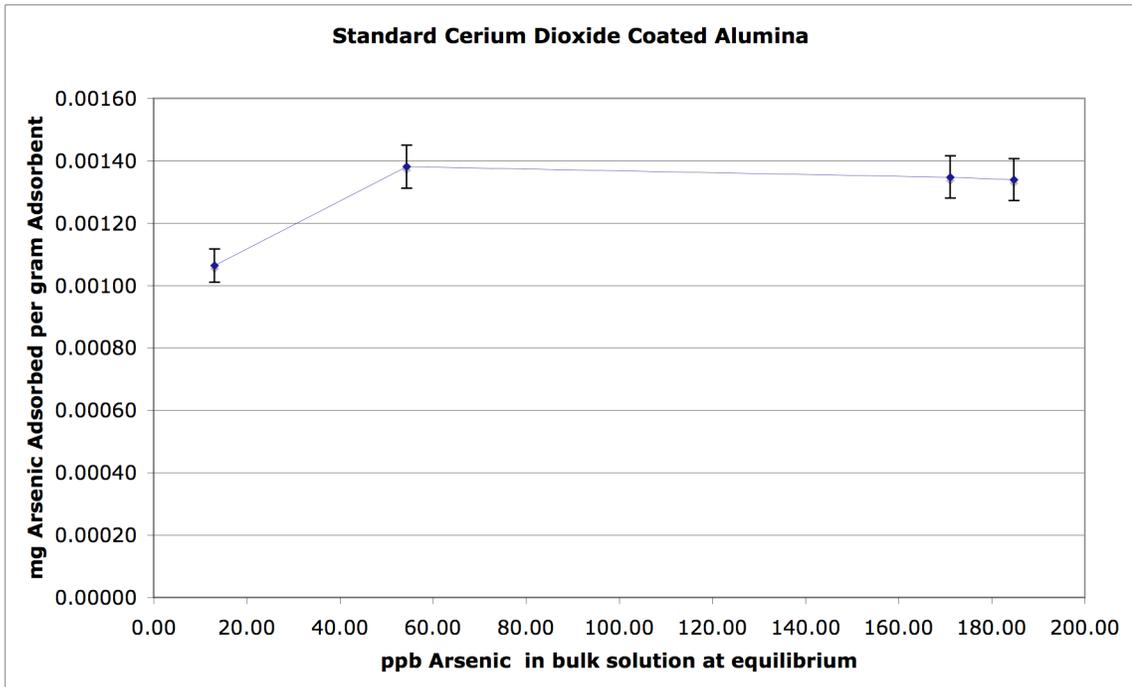
Figure 4.2-1, milligrams of arsenic adsorbed per gram of adsorbent (cerium dioxide coated alumina) vs ppb Arsenic in the bulk solution at equilibrium in order to construct a preliminary isotherm.

Figure 4.2-1 shows that originally there is an increase in the adsorption for an increase in solution concentration, which agrees with typical isotherm data in the literature (Cussler, 2009). However once the solution is approximately 250 ppb arsenic, the adsorption does not vary, implying that the adsorbent is saturated with arsenic at about 0.0014 mg Arsenic per gram of

Adsorbent. Although this shows a lower capacity than currently available adsorbents, these results can be used to help understand, and perhaps manipulate the environment and anticipate how the cerium dioxide will adsorb under a charity of conditions.

4.3 Adsorbent Regeneration

Since cerium is an expensive adsorbent and since most of the arsenic groundwater contamination problems reside in developing countries, there is a need to lower its cost (section 1). Peng et al. (2005) achieved a minimum of 80% regeneration of their cerium dioxide coated carbon nanotubes using various concentrations of a strong base, sodium hydroxide. A preliminary study of regeneration of cerium dioxide coated alumina adsorbent using the method of preparation outlined above following a similar method used in Peng (2005) yielded a 95% regeneration efficiency. This method was done adsorbing arsenic onto the particles following the procedure described in section 2.8, after the adsorption, the particles were removed from the water sample and 5 mL of NaOH (0.05M) was added to the particles. The particles with the base were shaken for 1 hour, filtered, and the NaOH sample was analyzed on the GF-AAS (Appendix A). Comparing the amount of arsenic removed from the first step, to how much arsenic was obtained in the basic solution, allowed us to determine the 95% regeneration efficiency. Further studies are needed to fully characterize the regeneration process, as it may be possible to achieve improvements in this already promising efficiency.

Chapter 5:

Summary and Conclusions

The purpose of this study was to determine if there was a cost effective way to study cerium dioxide as an adsorbent for arsenic removal, and if cerium dioxide coated alumina is a viable alternative to pure cerium dioxide adsorbent materials. Current arsenic removal techniques do not perform well enough to justify their cost and are too expensive to be used in developing countries. Although cerium dioxide is relatively expensive because of its rare earth component, it has exhibited promising removal efficiency in previous work. This study shows that the cerium coated alumina has a fraction of the adsorption capacity of the pure cerium dioxide adsorbent materials. Thus, it is not a viable alternative to the pure material as a practical adsorbent. However, it appears it may be useful as a laboratory analogue material; it exhibits adsorption behavior in response to environmental changes similar to the pure material but at a fraction of the cost.

This study was performed using a cerium dioxide nanoparticle grown directly on an alumina support. Although some current arsenic removal techniques use alumina as an adsorbent, alumina does not exhibit high adsorption rates or high efficiencies at various pH levels and high phosphate levels. Alumina was chosen as a support since it is already well studied for arsenic removal, but it is commercially available and provides an inexpensive support for the cerium dioxide nanoparticles.

In this study, cerium dioxide coated alumina was prepared in a number of ways, to assess how preparation affects arsenic removal. Results indicate that lower pH solutions used during the adsorbent synthesis yields adsorbent materials having higher adsorption capacities than the coated alumina prepared in a basic media. However, regardless of pH, the cerium dioxide coated nanoparticle adsorbents perform better than uncoated alumina. The study also reveals that a calcining temperature of 400C leads to better adsorbent than when calcined at 700C. It is

possible that the cerium dioxide coated alumina could be sintering at the higher temperatures and thereby having its effective surface area for adsorption reduced. Future work can focus on examining in more detail the chemical mechanisms that account for these trends, so perhaps they can be optimized to improve adsorbent performance.

Since current adsorption methods work best with pentavalent arsenic, a pretreatment step is needed to oxidize the trivalent to pentavalent arsenic. In order to reduce costs and craft a simpler adsorption process, using an adsorbent that does not need an oxidation step would be ideal. This study has shown that the cerium dioxide coated alumina works in both oxidized and reduced environments; this indicates that an adsorption process would not need a pretreatment step. Other important adsorbent characteristics are high capacities for arsenic as well as fast adsorption rates. The cerium coated alumina showed that all of the adsorption took place within the first hour; depending on the amount of cerium loaded onto the alumina, 95% of the arsenic could be removed in the first 5 minutes. Furthermore, it appears that the adsorbent capacity increases with increasing temperature. Mixing the cerium dioxide particles with other metal-coated alumina particles was also considered, and it was found that mixtures with calcium-coated alumina may provide advantages at high phosphate levels.

In this study the amount of cerium used to coat the alumina was chosen so that it would be 8x that required to fully coat the alumina particles if they were assumed to be spherical in shape and with no pores. Such adsorbents showed roughly 80% adsorption of a 250 ppb arsenic sample after 1 hour using a batch process. When the adsorbent was created with a 16x concentration, the adsorption rates were similar to those for a pure cerium dioxide nanoparticle (from Sigma Aldrich, 25 nm). Simple estimates based on the 16x solution of cerium dioxide suggest that the cerium dioxide coated alumina would cost 25 times less than a pure cerium dioxide adsorbent system. This suggests that cerium dioxide nanoparticles coated on an alumina particle substrate may be attractive as a low cost alternative to pure cerium-dioxide nanoparticles in studying the effects of adsorption.

It is hypothesized that the low adsorption capacity of the cerium dioxide coated alumina particles is a result of the low surface area of the alumina particles themselves. Future work should focus on coating the cerium dioxide nanoparticles on alumina or activated carbon supports. These supports have much higher surface areas than the alumina particles of this study and potentially could increase the adsorption sites for arsenic on the coated adsorbent. Coupled with the various adsorption trends elucidated in this study, this improvement in capacity could make cerium-dioxide a cost effective and robust adsorbent suitable for arsenic removal under a variety of ambient groundwater conditions.

Appendix A

The Detection Method for Arsenic

A.1.1. Survey of Detection Methods

The detection of arsenic in ground water used for human consumption has become routine. Stringent water quality standards and guidelines require the analysis and detection of arsenic at trace levels. (Ahmed, 2007) Since the Environmental Protection Agency (EPA) has moved the acceptable arsenic concentration limit from 50 ppb (or 0.05 mg/L) to 10 ppb (0.01 mg/L), a technique is required to determine arsenic concentration accurate to 1 ppb. Since many of the water samples that need to be analyzed contain other ions, the method must not be affected by changes in other materials. Furthermore, arsenic samples are dissolved in an aqueous medium (ground water) and thus a preferred detection method should require no pretreatment before solution concentrations are determined.

There are a variety of analytical techniques for bench-scale detection of arsenic. The most prevalent methods are Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma (ICP), Anodic Stripping Voltammetry (ASV), and Silver Diethyldithiocarbamate (SDDC) spectrometric methods (Ahmed, 2007). AAS is a sensitive single-element technique that is well studied and is very reproducible and user friendly. Both Hydride Generation (HG) and Graphite Furnace (GF) AAS methods are widely used for analysis of arsenic in water due their ability to detect trace amounts. Another very well know method is also reproducible is ICP Atomic Emission Spectrometry (AES) and Mass Spectrometry (MS). Both ICP methods can detect multiple elements at the same time unlike the AAS. The two previous mentioned methods, ASV and SDDC are useful and lower in cost than the ICP or AAS methods, but they both are not very

reproducible. (Ahmed, 2007). A summary of these techniques, their detection ranges, the

required size of a sample, and costs are provided in Table A-1.

	Limit (ug/L)	Size (mL)	Cost ($1000)	
HG-AAS	0.05-2	50	20-100	Single element
GF-AAS	1-5	1-2	30-100	Single element
ICP-AES	35-50	10-20	60-200	Multielement
ICP-MS	0.02-1	10-20	150-400	Multielement
ASV	0.1-2	25-50	5-20	Only free dissolved arsenic
SDDC	1-10	100	2-10	Single element

Table A-1: Summary table for detection methods, their detection limits, sample size and
approximate costs to measure trace concentrations of arsenic.

It should be noted that current field test kits for arsenic invoke chemical reactions (not the

techniques shown Table A-1), and are typically single use, have detection limits as low as 10 ppb,

and cost $40-$100 per use. The results obtained by arsenic field test kits are very much

dependent on the type and quality of chemicals in the kit, sample preparation, the quality of

water, and are prone to human error. Therefore, field test are not reliable enough for the purposes

of scientific inquiry.

A.1.2. The GF-AAS Technique

In this study GF-AAS was utilized because it allows for analysis detection of arsenic in

the low ppb range, and the sample size needed is only 1-2 mL. All of the arsenic analysis was

done by a Perkin-Elmer Spect800 GF-AAS. To ensure consistent results, *Method 200.9*

published by the US Environmental Monitoring Systems Laboratory was used.

AAS is a method that can quantitatively determine the elemental compositions of a

mixture by observing the light emitted by free atoms in their gaseous states. All AAS methods

depend on the established science that that free atoms absorb light at different frequencies

characteristic of the element of interest. Most samples can be broken down into free elements at

high temperatures. Within certain detection limits, the amount of light absorbed by the element

can be linearly correlated to the concentration of the sample present after calibrating the instrument with standards of known concentrations.

In the GF-AAS, the method chosen in this study, a graphite coated furnace tube is used to vaporize the sample (at approximately 2,000 degrees Celsius). GF-AAS instruments have 5 basic features: 1) a source of light, 2) the graphite tube in which the sample is vaporized, 3) a monochromator for selecting one wavelength (visible or ultraviolet) for the element of interest, 4) a detector, typically a photomultiplier tube that measures the amount of absorption, and 5) a computer based system to analyze the data.

Further information on GF-AAS theory and set-up relevant to the current study can be found in the PerkinElmer Atomic Spectrometry booklet on the THGA Graphite Furnace Techniques and Recommended Conditions, Release 3.0. This booklet contains recommended operating conditions to measure arsenic compositions, including wavelength, slit widths, pretreatments temperatures, and atomization temperatures. The booklet also contains information on modifiers and sensitivity checks to create reproducible data. (Modifiers allow the ample to reach higher temperatures before charring and increases probability that the element will decompose in the gaseous state).

A.1.3. GF-AAS in the Current Study

To be consistent with other methods of detection used in papers referenced in this study, each arsenic solution sample was analyzed on the GF-AAS at least 3 times after contacting the adsorbent. Furthermore, each experiment was repeated 3 times for each data point given on the reported data. Therefore the reported values of arsenic adsorption data points correspond to an average of at least 9 values.

Each time the furnace tube was replaced (approximately every 50 samples) a new calibration curve was generated. The calibrations range was 0-250 ppb Arsenic (points every 12.5 ppb or 0.0125 mg/L), and curves were obtained with varying concentrations of phosphates

(0-25,000 ppb) and HEPEs (0.015M). It was found that the addition of these latter two chemicals did not affect the calibration curve.

Before each set of experimental samples was analyzed, a blank (0 ppb arsenic) and a 250 ppb arsenic standard were analyzed by the GF-AAS to assure calibration and accuracy of the results. Day to day relative error that occurred on the AAS, including changing of the furnace tube, was no more than 1% based on the calibration curves. Since the error was low and data reproducible, the GF-AAS was deemed acceptable for determining the concentration of the arsenic in this study. All GF-AAS measurements presented in this study can be assumed to be accurate to 1% and thus variations in repeated data sets larger than this are due to other experimental sources of error.

Appendix B

Chemical Information

B.1 Preparation of Coated particles

Although the amount of adsorbent prepared varied depending on anticipated use, the proportions of all components listed below stayed the same. Cerium dioxide coated nanoparticles were synthesized and coated on the alumina substrate in the same solution at the same time. The procedure for doing so was as follows:

Added 150mL of 18mΩ deionized water, to 5 grams Alumina 325 mesh

While stirring heated to ~40C using a water bath, pH= ~8.5

Added 10x 0.1M of the $Ce(NO_3)_3$ solution (described below)

Added a small amount of citric acid until pH = ~4

Added Ammonium Hydroxide until pH = ~5

Added 11x 0.025 mL of a 0.5% Hydrogen peroxide solution (pH ~5.5)

Using the water bath, heated and stirred for 45 minutes at ~60C

Stirred an additional hour at room temperature (solution may turn yellow)

Allowed to settle over night or at least 12 hours

Decanted excess liquid, placed in muffle furnace at 400C for 1 hour

For Basic procedure (used in Section 2.6) same as above except:

No Citric Acid was use, and Ammonia Hydroxide was added until pH 10

Calcium and Iron coated alumina adsorbents:

The Iron and Calcium samples described below were used instead of the $Ce(NO_3)_3$ solution; since molarities were the same, the same solution volume was added.

For Cerium Dioxide Coated 100 mesh coated Alumina

Same procedure as above, but 5 grams of the 100 mesh alumina was used

B.2 Chemical Lot numbers and Stock Solutions

The following are the lot numbers and chemical standards that were used in this study.:

Alumina Oxide, 100 mesh 99%, Sigma Aldrich, Lot #03996TJ

Alumina Oxide, 325 mesh 99+%, Sigma Aldrich, Lot # 20950

Ammonium Hydroxide, GR ACS, Lot # 49296

Arsenic, AAS Standard, Fluka Analytical Lot #1406015

Calcium Chloride Dihydrate, Granular, J.T. Baker #08530

Citric Acid MonoHydrate Powerder, Sigma Adrich Lot# 0122-01

Cerium Nitrate HexaHydrate, Sigma Aldrich Batch #12424BE

Cerium (IV) Oxide Nanopowerder <25nm Aldrich, # MKBB9545

Disodium Phosphate, Acrosorganics Lot # AO283583

HEPEs, free acid: EMD Chemicals Lot # R060166

Iron Nitrate pentaHydrate, Sigma Aldrich Lot# MKBB4806

Mg Modifier 10,000 mg/L Perkin-Elmer AA Modifier solution BO 190634 (see

preparation below)

Monosodium Phosphate, MP Biomedicals Lot #7386H

Pd Modifier 10,000 mg/L Perkin-Elmer AA Modifier solution BO 190 635 (see

preparation below)

Sodium Chloride Crystals, J.T. Baker # 7647-15-5

Preparation of Pd Modifier for GF-AAS

1mL of the modifier solution was diluted into a 10mL volumetric flask with 18mΩ deionized water. 5uL of this solution was added to each injection on the GF-AAS.

Preparation of Mg Modifier for G-AAS

1mL of the modifier solution was diluted into a 10mL volumetric flask with 18mΩ deionized water. 3uL of this solution was added to each injection on the GF-AAS.

Preparation of Phosphate Buffer (10,000,000ppb Phosphate)

For a pH of ~7, used 2.62 grams Monosodium phosphate, and 4.13 grams of Diosodium phosphate, diluted in 100mL volumetric flask with 18mΩ deionized water.

Preparation of Arsenic water samples

Using volumetric flasks, appropriated mass of HEPEs buffer was added to make a 0.015M solution, appropriate dilution of the above Phosphate buffer was added to make the solution contain the correct phosphate level (0-25,000 ppb dependent on trial), and appropriate dilution of the Arsenic AAS standard to get correct ppb Arsenic (for almost all experiments arsenic concentration was 250ppb). Since arsenic concentration may be affected in the presence of Silicon dioxide, all preparation and storage was done in plastic containers, using plastic pipettes.

Preparation of Cerium Nitrate Solution

0.0865grams of the $Ce(NO_3)_3 \cdot 6H_2O$ was added into 10 mL of 18mΩ deionized water.

Preparation of Iron Nitrate Solution

0.0808grams of the $Fe(NO_3)_3 \cdot 9H_2O$ was added into 10 mL of 18mΩ deionized water.

Appendix C

Surface Studies

C.1 Studies of Cerium Dioxide Surface and Arsenic species

Cerium (IV) oxide, is also commonly known as ceria or cerium dioxide, corresponding to its oxidation level of +4. Cerium can also form a second oxide with its oxidation level +3, called cerium (III) oxide.. Cerium (IV) oxide is the most stable at room temperature and under atmospheric conditions. The base structure of cerium dioxide is a cubic fluorite lattice or a face-centered-cubic, with a cell constant of a=5.411 Angstrums with four cerium atoms per unit cell (Conesa, 1995). These values were used in the approximate calculations in Appendix D.

The most stable surface for the cerium dioxide is its (111) face (Conesa, 1995), which is expected since it is the most compact. All the exposed cerium ions are seven-coordinated and all surface oxygen ions are bonded to three Cerium ions (Conesa, 1995) with the exposed oxygen atoms bound to only 1 cerium. The oxygen atoms on the surface become OH^- groups when they are calcined. The oxidation state of the cerium (+3 or +4) determines how basic the oxygen will be (oxygen on a +4 cerium will be less basic than an oxygen on a +3 Cerium).

Arsenic in water typically takes on two different forms, either in its trivalent (+3) or pentavalent (+5) state. Although arsenic can also take on oxidation levels of 0 -3, these are less common and are not relevant to groundwater purification. In water, arsenic forms a compound with hydrogen and oxygen, either H_3AsO_4 (+5) or H_3AsO_3 (+3). The pH and the local oxygen concentration will determine which species of arsenic will form.

Appendix D

Calculations

D.1 Estimate of Cerium Dioxide quantity necessary to coat 325 mesh Alumina

The following calculation was performed to determine the amount of cerium dioxide needed to completely coat the surface of alumina, assuming that the alumina is spherical in shape. Although it is acknowledged that the alumina is likely not spherical, this calculation provides a good starting estimate for solution concentrations necessary to achieve complete loading of alumina particles by the cerium dioxide.

Calculation:

325 Mesh alumina has an average particle diameter of 0.045mm

Surface Area of Alumina Calculation :
$$SA = 4 \cdot \pi \cdot r^2 = 4 \cdot \pi \cdot (0.0000225m)^2 = 6.362 \cdot 10^{-9} m^2$$

Volume of Cerium Dioxide coating (Assuming a $5\overset{o}{A}$ thickness) :
$$Vol = (thickness) \cdot (SA) = (5\overset{o}{A}) \cdot (6.362 \cdot 10^{-9} m^2) = 3.181 \cdot 10^{-18} m^3$$

Assume the density of Cerium Dioxide is 6.9g/cm³

Mass of Cerium Dioxide per 325 mesh Alumina Particle :
$$Mass/Particle = (density) \cdot (volume) = (6.9g/cm^3) \cdot (3.181 \cdot 10^{-18} m^3) = 2.195 \cdot 10^{-11} gCeO_2 / \text{Alumina Particle}$$

Assume density of Alumina is 3.97g/cm³

Volume of Alumina Particle :
$$Vol = 4/3 \cdot \pi \cdot r^3 = 4/3 \cdot \pi \cdot (0.0000225)^3 = 4.771 \cdot 10^{-14} m^3$$

Volume of 1 g Alumina $2.52 \cdot 10^{-7} m^3$

Number of Alumina Particles/gram
$$Particles/gram = \frac{\text{vol in 1 gram}}{\text{vol of particle}} = \frac{2.52 \cdot 10^{-7} m^3}{4.771 \cdot 10^{-14} m^3} = 5.282 \cdot 10^6 \, particles/gram$$

Mass of CeO_2 needed to cover 1 gram of Alumina :
$$particles/gram \cdot mass \, CeO_2/particle = 5.282 \cdot 10^6 \, particles/gram \cdot 2.195 \cdot 10^{-11} gCeO_2 / \text{Alumina Particle}$$
$$= 1.1592 \cdot 10^{-4} gCeO_2 / gAlumina$$

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