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Arsenic Water Technology Partnership

Aerogel & Iron-Oxide Impregnated Granular Activated Carbon Media For Arsenic Removal

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The Awwa Research Foundation (AwwaRF) is a member-supported, international, nonprofit organization that sponsors research to enable water utilities, public health agencies, and other professionals to provide safe and affordable drinking water to consumers.

The Foundation's mission is to advance the science of water to improve the quality of life. To achieve this mission, the Foundation sponsors studies on all aspects of drinking water, including supply and resources, treatment, monitoring and analysis, distribution, management, and health effects. Funding for research is provided primarily by subscription payments from approximately 1,000 utilities, consulting firms, and manufacturers in North America and abroad. Additional funding comes from collaborative partnerships with other national and international organizations, allowing for resources to be leveraged, expertise to be shared, and broad-based knowledge to be developed and disseminated. Government funding serves as a third source of research dollars.

From its headquarters in Denver, Colorado, the Foundation's staff directs and supports the efforts of more than 800 volunteers who serve on the board of trustees and various committees. These volunteers represent many facets of the water industry, and contribute their expertise to select and monitor research studies that benefit the entire drinking water community.

The results of research are disseminated through a number of channels, including reports, the Web site, conferences, and periodicals.

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This study was jointly funded by the Awwa Research Foundation (AwwaRF) and the U.S. Department of Energy (DOE) under Grant No. DE-FG02-03ER63619 through the Arsenic Water Technology Partnership. The comments and views detailed herein may not necessarily reflect the views of the Awwa Research Foundation, its officers, directors, affiliates or agents, or the views of the U.S. Federal Government and the Arsenic Water Technology Partnership. The mention of trade names for commercial products does not represent or imply the approval or endorsement of AwwaRF or DOE. This report is presented solely for informational purposes.

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FOREWORD

The Awwa Research Foundation is a nonprofit corporation that is dedicated to the implementation of a research effort to help utilities respond to regulatory requirements and traditional high-priority concerns of the drinking water community.

The Arsenic Water Technology Partnership (AWTP) program is a partnership between AwwaRF, Sandia National Laboratories (SNL) and WERC, a Consortium for Environmental Education and Technology Development at New Mexico State University that is funded by DOE and the Awa Research Foundation. The goal of the program is to provide drinking water utilities, particularly those serving small and rural communities, with cost-effective solutions for complying with the new 10 ppb arsenic MCL. This goal is being met by accomplishing three tasks: 1) bench-scale research to minimize operating, energy and waste disposal costs; 2) demonstration of technologies in a range of water chemistries, geographic locales, and system sizes; and 3) cost effectiveness evaluations of these technologies and education, training, and technology transfer.

The AWTP program is designed to bring new and innovative technologies developed at the laboratory and bench-scale to full-scale implementation and to provide performance and economic information under actual operating conditions. Technology transfer of research and demonstration results will provide stakeholders with the information necessary to make sound decisions on cost-effective arsenic treatment.

AwwaRF participates in the overall management of the program, helps to facilitate the program's oversight committees, and administer the laboratory/bench-scale studies. SNL conducts the pilot-scale demonstrations and WERC oversees the education, training, economic analysis, and outreach activities associated with this program.

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The authors wish to acknowledge the involvement of Sabre Coleman from Lawrence Livermore National Laboratory for assistance on the initial proposal and providing samples of aerogel-GAC materials. The City of Scottsdale provided access to its groundwater wellsites and historic data which was valuable throughout this project. Paul Sylvester and Owen Boyd (Solmetex Inc.) generously provided their technical assistance and time to develop a marketable Fe-GAC product.

Much of the laboratory work was conducted by Jorge Christian Navarro Aragon at Arizona State University, who received his Masters of Science in Engineering degree in December 2005. Further assistance from Andrew Baumgardner and Mohammad Badruzzaman at ASU is appreciated, as is research by a visiting student (Renaud Bordier) from the University of Poitiers (France). Additional gratitude is extended to the graduate students (Wei Cheng, Abhishek Yadav, and Zaheer Sheikh) and post-doctoral researchers (Dr. Seyed Dastgheib and Dr. Yanping Guo) at Clemson University.

Technical advice and guidance of the AwwaRF project officer, Albert Ilges, is appreciated.

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RESEARCH OBJECTIVES

The goal of this project is to validate proof-of-concept testing for iron enriched granular activated carbon (GAC) composites (aerogel-GAC or iron-oxide impregnated) as a viable adsorbent for removing arsenic from groundwater and conduct technical and economic feasibility assessments for these innovative processes. Specific project objectives include:

- Conduct batch experiments for aerogel-GAC and Fe-oxide impregnated GAC composites to evaluate their performance removing arsenic.
- Evaluate Fe-GAC media performance in rapid small scale column tests (RSSCTs) to assess arsenic removal in a more dynamic treatment system.
- Evaluate Fe-GAC potential for removal of other contaminants (e.g., methyl tertiary butyl ether, dissolved organic carbon).
- Characterize Fe-GAC media.
- Correlate performance and media characterization for possible selection of two media for a future second phase of this project.

APPROACH

Three different techniques to impregnate iron onto GAC was evaluated: 1) iron containing aerogel impregnation of GAC (Lawerence Livermore National Laboratory); 2) four methods of impregnating iron oxides or zero valent iron onto GAC (Clemson University); 3) impregnating iron hydroxide onto GAC (Solmetex Inc. & ASU). Iron content of each sample was determined before conducting batch adsorption experiments and/or column tests. Effects of water chemistry (pH, competing ions) and operating conditions (empty bed contact times) were evaluated. Co-removal of arsenic and synthetic organic chemicals (MTBE and benzene) were evaluated.

CONCLUSIONS

- Fe-GAC composite media contained <1% to 15% iron by dry weight. There were no friability issues during use of the media, nor did iron appear to "flake" off of the composite media. Thus Fe-GAC media appear suitable for batch or packed-bed use during water treatment.
- Arsenic removal by Fe-GAC composites depended highly upon the process used to impregnate iron. Iron-aerogel materials had the lowest iron content and exhibited the lowest arsenic adsorption capacities. Roughly six other techniques to impregnate iron into GAC were successful and were the focus of the study. For these materials iron impregnation did not alter the surface area significantly (<15% change), as measured by nitrogen deposition. However, arsenic adsorption varied significantly based upon the technique to impregnate iron.
- Arsenic adsorption was not a function of the iron content (i.e., mgFe/mgGAC). This implies that the technique to impregnate Fe-GAC composites and the resulting mineralogy and structure is probably more important than the iron content.
- The best performing Fe-GAC composite for As(V) from Clemson University (C-II4 and C-II4B) was produced via an iron hydroxide precipitation process. This was superior to

iron impregnated via ion exchange, organic-ligand based, or zero valent iron based techniques. The zero valent iron based technique result achieved comparable or slightly better As(III) removal than other Clemson University Fe-GAC composites.

- The best overall performing Fe-GAC composite was synthesized by Arizona State University and Solmetex Inc. using a patented process. Generally, this process involves in-situ precipitation of iron (hydr)oxide using an oxidant and reduced iron species.
- Extensive media characterization was undertaken (surface area, pore size distributions, zeta potential, and various spectroscopy measurements). These proved valuable in assessing differences between iron deposition techniques.
- Batch kinetic experiments indicated that 100x140 mesh Fe-GAC composites reached pseudo-equilibrium for As(V) adsorption within 7 days of contact time. Adsorption isotherms were fit well by the Freundlich Isotherm model ($q = KC_e^{1/N}$).
- In batch experiments with Fe-GAC composites, As(V) adsorption improved as solution pH decreased. For example, the adsorptive capacity constant (K) decreased by a factor of ten for each full pH unit increase, between pH 5 and 9.
- In batch experiments with Fe-GAC composites and silicate (20 ppm) at pH 6.5 and 8.5, addition of silicate decreased As(V) adsorption at both pH levels. All Fe-GAC composites evaluated exhibited similar pH, silicate, vanadate and other competing ion effects.
- In batch and column experiments with Fe-GAC composites, As(V) adsorption was lower in groundwaters or NSFI-53 challenge water compared model solutions prepared from nanopure water at an equivalent pH as the groundwater. Thus, ions present in these more complex water matrices compete for arsenic adsorption sites on the Fe-GAC composite. Addition of 100 ppb vanadate to the NSFI-53 challenge water had almost no effect on As(V) removal. Addition of 20 ppm silicate to the NSFI-53 challenge water decreased As(V) adsorption at both pH 6.5 and 8.5, compared against the NSFI-53 challenge water prepared without silicate added. Thus silicate appears to be a major foulant/competitor for As(V) adsorption sites on Fe-GAC.
- In batch and column tests, decreasing the ionic strength of a groundwater through blending with nanopure water resulted in improved As(V) adsorption. These experiments maintained the same ratio of ions, but demonstrate that the concentration of competing ions affect As(V) adsorption.
- Rapid small scale column tests (RSSCTs) were conducted in continuous flow operation with empty bed contact times (EBCTs) of 2.5 to 10 minutes. Fe-GAC composites that performed best in batch testing, also had the best performance in RSSCTs. The ASU and Solmetex Inc. Fe-GAC composites achieved the longest run length (i.e., bed volumes treated). Lengthening the EBCT resulted in a larger number of bed volumes treated. The minimum EBCT recommended EBCT is 4 minutes; at 2.5 minute EBCT the mass transfer zone was not captured within the column.
- RSSCTs operated for 50,000 to over 100,000 bed volumes before complete As(V) breakthrough.
- RSSCTs were also conducted with a surface water containing dissolved organic carbon (DOC) and model groundwaters spiked with MTBE and benzene. Both waters also contained As(V). As(V) was removed effectively, and did not seem to be impacted by the presence of DOC, MTBE or benzene. Fe-GAC removed not only the As(V), presumably due to adsorption onto iron (hydr)oxides, but also removed the DOC and

synthetic organic chemicals (MTBE and benzene). Organics were presumably removed by adsorption onto the GAC. Therefore, iron impregnation does not appear to hinder organic removal by GAC, but adds the capability to remove arsenic.

- GAC is a relatively inexpensive substrate to impregnate with iron. For water treatment situations were co-removal of arsenic and other contaminants suitable for removal by GAC is desired (e.g., SOCs, radionuclides, DOC) Fe-GAC composites are a feasible option.

RECOMMENDATIONS FOR FUTURE RESEARCH

- Optimization of the selection of base GAC substrate and iron deposition process needs to be conducted. This should follow the basic technique which resulted in the best performing Fe-GAC composites (produced by ASU and Solmetex Inc.).
- Batch equilibrium tests proved to be excellent indicators of more labor-intensive RSSCT performance. Future work should use batch tests to screen new composites. However, optimization of Fe-GAC composites must also consider that deeper iron penetration into the GAC base material may impact arsenate mass transfer. Therefore, RSSCTs should continue to be conducted to assess mass transport limitations.
- Because Fe-GAC composites are new materials, there is a need to compare arsenic breakthrough achieved from pilot tests against those achieved by RSSCTs to validate the scaling approach.
- Improved spectroscopic analysis of Fe-GAC composites is warranted to understand the nano-structure of the iron deposits (coated surface versus crystals crossing through the pore space). This could help optimize the iron deposition process (e.g., duration of iron treatment). Ultimately the goal should be to maximize iron content for the best iron mineralogy to result in the most arsenic removal.
- Forensic analysis of spent media would provide additional insight into the role of foulants and changes in mineralogy over time.
- A detailed economic analysis of iron-oxide impregnated GAC composites should be conducted. Without full-scale production of these products the economic analysis could be conducted based upon costs of raw materials, costs for similar processes applied for other products, and lifecycle cost of the media.

CHAPTER 1 INTRODUCTION AND OBJECTIVES

STATEMENT OF PROBLEM

Arsenic is a ubiquitous metalloid that naturally occurs in surface and groundwaters. The speciation of arsenic depends on the pH and redox potential (e.g., Eh) of the water body. Arsenic usually occurs as arsenate [As(V)] or arsenite [As(III)] in potable water supplies. Arsenate (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, or AsO_4^{3-}) is typically present in the mono- and divalent anionic forms in oxygenated waters while arsenite (H_3AsO_3, $H_2AsO_3^-$, and $HAsO_3^{2-}$) occurs primarily in the neutral and in lower Eh waters. Arsenic is classified as a human carcinogen (prone to cancer of the bladder, lungs, skin, kidney, liver, and prostate) by the International Agency for Research on Cancer and the National Research Council (NRC, 1999, 2002; Pontius et al., 1994). In 2002, the USEPA lowered the maximum contaminant level (MCL) for arsenic in drinking water from 50 μg/L to 10 μg/L, and the new MCL became effective in January 2006 The WHO, the European Union, and several countries recently lowered the recommended or required arsenic limit to 10 μg/L. Because of the lower MCL, potable water suppliers have an increased need for arsenic removal processes suitable for treating water sources with low ambient arsenic concentrations (10 to 50 μg/L).

Arsenic can be removed from surface and groundwater supplies by iron or alum coagulation with filtration, reduced Fe/Mn oxidation systems, and lime softening (Cheng, Wang et al. 1994; McNeill and Edwards 1995; Scott, Green et al. 1995; Hering, Chen et al. 1997; McNeill and Edwards 1997; Chen, Fields et al. 2002). Anion-exchange resin and activated alumina packed-bed systems are traditionally used for wellhead or point-of-entry groundwater treatment systems (Lin and Wu 2001; Wang, Chen et al. 2002). In recent years, several iron-based adsorbents have been developed that typically require less chemical pretreatment and/or can treat a greater number of bed volumes than anion exchange resins or activated alumina. Porous iron oxide or hydroxide (GFH, Bayoxide E33) packed-bed adsorbent systems are used in Europe for arsenic treatment (Jekel and Seith 2000). Zero valent iron (ZVI) systems are used for in-situ and above ground arsenic mitigation (Lackovic, Nikolaidis et al. 2000; Farrell, Wang et al. 2001; Su and Puls 2001; Bang, Meng et al. 2002; Manning, Hunt et al. 2002; Meng, Bang et al. 2002). The porous nature of the iron oxides/hydroxides presumably results in arsenic adsorption at internal iron complexation sites, whereas ZVI relies on iron corrosion, reprecipitation, and arsenic adsorption on the external surface of the adsorbent. Bench-scale comparisons of porous and non-porous iron, sulfur-modified iron, and activated alumina adsorbents for arsenic removal suggest a large number of newly developed adsorbents may be economically feasible in achieving the new arsenic MCL (Sinha, Lee et al. 2002).

Iron has a high affinity for arsenic and forms strong inner-sphere complexes. Based on the literature, iron (hydr)oxides have pK_{a1} and pK_{a2} values of ~7.3 and 8.9, respectively, resulting a pH_{ZPC} on the order of 8.1. Coulombic forces favor association of anionic arsenate with positive surface sites (e.g., $MeOH_2^+$). Arsenic adsorption onto TiO_2 has not yet been modeled, but probably mirrors other inner-sphere metal (hydr)oxide surface site (SOH) complexes with arsenic:

$$\equiv FeOH_2^+ \leftrightarrows \equiv FeOH + H^+ \qquad pK_{a1} \tag{1.1}$$
$$\equiv FeOH \leftrightarrows \equiv FeO^- + H^+ \qquad pK_{a2} \tag{1.2}$$
$$SOH + H_3AsO_4 \leftrightarrows SAsO_4^{2-} + H_2O + 2H^+ \tag{1.3}$$
$$SOH + H_3AsO_3 \leftrightarrows SAsO_3^- + H_2O + H^+ \tag{1.4}$$

In addition to this electrostatic bonding between arsenic species and mineral surfaces, arsenic will also form covalent bonds with some surfaces. These include monomolecular monodentate and monomolecular bidentate bonds. Whereas electrostatic bonds form rapidly (seconds) and depend on the charge difference between the arsenic and the surface, covalent bonds depend on their respective molecular structure and form less rapidly. Covalent bonds are stronger (i.e., irreversible) than electrostatic attractions. As covalent bonds form, surface sites can become available for electrostatic bonding again. The kinetics of bond formation may affect the optimal contact time required for a specific media in a column operation. Overall, media taking advantage of the strong affinity between arsenic and iron will lead to good treatment strategies.

This project involves a new array of granular activated carbon (GAC) based adsorbents that contain iron for arsenic removal. GAC has low capacity for arsenic, but provides a porous substrate to which iron or iron compounds can be added. Iron enriched GAC would remove both arsenic and organics (VOCs, SOCs, DOC). By combining the benefits of GAC and iron (hydr)oxides a new class of arsenic adsorption media can be developed with the following benefits:

- GAC has much higher surface area (700-1200 m^2/g) than commercially available metal oxide media (GFH (226 m^2/g), E33 (130 m^2/g), FS-50 (232 m^2/g), iron-modified AA (161 m^2/g) and activated alumina (265 m^2/g)). The higher GAC surface area has the potential for a larger number of arsenic adsorption sites.
- Iron enriched GAC (Aerogel or iron-oxide impregnated) will simultaneously remove VOC's, SOC's, uranium, and potentially radionuclides in addition to arsenic
- Iron enriched GAC (Aerogel or iron-oxide impregnated) have apparent densities of ~0.6 g/cc and are lower than metal oxides (~1.5 g/cc), so less absolute mass of GAC is required to fill a packed-bed vessel of a given size.
- Commercial iron-oxide adsorbents cost between \$4/lb to \$8/lb, whereas GAC substrate is < \$1/lb and the cost of iron enrichment will probably mean a less expensive product.
- Iron enriched GAC can be manufactured to optimize iron content
- Aerogel-GAC composites are a new and novel treatment process that maintains a high porosity and high surface area; iron-oxide impregnation also maintains most of the surface area.
- Iron enriched GAC can be distributed via a well developed GAC process platform or replace media in existing metal-oxide packed bed treatment systems.

- Aerogel-GAC composites can be optimized for high arsenic selectivity (low competition by competing ions) by changing the ratio of Fe/Mn content
- Aerogel-GAC composites can serve as a platform product and aerogel could be reformulated to remove other contaminants (hexavalent chromium, perchlorate)
- The infrastructure for GAC supplies, markets, treatment infrastructure (vessels, pumps, handling, etc), and disposal is very well established and would provide rapid deployment (market penetration) of iron-modified GAC composites into the water industry.

PROJECT OBJECTIVES

The goal of this project is to validate proof-of-concept testing for iron enriched granular activated carbon (GAC) composites (aerogel-GAC or iron-oxide impregnated) as a viable adsorbent for removing arsenic from groundwater and conduct technical and economic feasibility assessments for these innovative processes. Specific project objectives include:

- Conduct batch experiments for aerogel-GAC and Fe-oxide impregnated GAC composites to evaluate their performance removing arsenic.
- Evaluate the best GAC media performances in rapid small scale column tests (RSSCTs) to assess arsenic removal in a more dynamic treatment system.
- Evaluate Fe-GAC potential for removal of other contaminants (e.g., methyl tertiary butyl ether, dissolved organic carbon).
- Characterize spent Fe-GAC media.
- Correlate performance and media characterization for possible selection of two media for a future second phase of this project.

CHAPTER 2 EXPERIMENTAL AND ANALYTICAL METHODS

This chapter describes the types of media used for batch and column experiments. Details of analytical methods are also presented. All laboratory waters were prepared using nanopure water (NANOpure Infinity Ultra-pure Water System).

IRON MODIFIED MEDIA

Clemson University provided 17 different iron-impregnated GAC samples to ASU. Norit HD3000 carbon was acid washed, heat or steam treated, and sieved prior to iron treatment. These 17 samples were prepared using four different preparatory approaches, plus control samples without iron impregnation (Table 2.1). All materials provided to ASU were 100x140 mesh. Table 2.1 shows the Fe-GAC composites prepared by Clemson University with the different iron impregnation processes. Coal-based mesoporous GAC HD3000 (Norit Inc.) was used as precursor material in this study. The different Fe-GAC samples were assigned acronyms based upon the institution preparing the sample ("A" represents Arizona State University; "C" represents Clemson University; "L" represents Lawerence Livermore National Laboratory; "S" represents Solmetex Inc.) and an internal sample identification code. The majority of samples were prepared using a single, common base GAC material (HD = Norit HD3000); for one set of samples a second GAC material was used (Jacobi Carbons Ltd.).

Clemson University prepared all samples using acid washed Norit HD3000 material (sample C-1). Some samples were also pretreated using heat (HDHT; sample C-2) or stream (HDST; sample C-7). Then four different types of iron impregnation were undertaken using these materials:

I. Ion exchange technique (HDHTFeS): acid-washed and heat treated Norit HD3000 was mixed with $FeCl_3$. The solution was evaporated at 800 ^oC under a nitrogen gas flow stream.

II. Iron hydroxide precipitate technique (HDHTFeOH): acid-washed and heat- or steam- treated Norit HD3000 was mixed with an aqueous $FeCl_3$ solution. The pH of the solution was increased to either pH 9 or 11 using sodium hydroxide and then filtered. Another sample (HDHTFeOHI) was prepared in a same fashion, but the GAC but carbon was separated from iron solution before immersing in a 0.1N NaOH solution followed by filtration, washing and drying.

III. Organic-iron complexed technique (HDHTFeOX): acid-washed and heat treated Norit HD3000 was mixed with and organic-iron complex solution in the presence of hydrochloric acid. After exposure to the solution, moisture was evaporated at 800 ^oC.

IV. Zero valent iron technique (HDHTFe^0): acid-washed and heat treated Norit HD3000 was mixed with $FeCl_3$. Then the solution underwent wet chemical reduction prior to filtration. Another sample (HD-16NOFe2A) was prepared by mixing $FeSO_4$ solution under nitrogen atmosphere, followed by air oxidation under controlled pH (HD,16NOFe2A).

After preparation, all of the samples were extensively washed with distilled and deionized water until no iron could be detected in the filtrate, then dried at 90°C for samples treated by I and II and 40°C for III and IV. After sieving, a 100x140 mesh size was used for the experiments. Later in the project Clemson University produced three new Fe-GACs (C-16A-3, C-17A-3 and C-IV13B-6). These new media were designed based upon the results of characteristics of C-II4-11 and C-IV13.

Solmetex Inc. and Arizona State University prepared a second set of materials used a different process for depositing iron and is based on its patent license to impregnate iron on to ion exchange resin (i.e., ArsenXnp media). This Solmetex iron-deposition process produced four Fe-GAC samples, all with 12x60 mesh sizes. The 12x60 mesh size material was crushed and sieved to 100x140 mesh. Table 2.2 presents Fe-GAC composites manufactured by Solmetex and ASU following the patented process of Solmetex. HD3000 GAC was the base for all composites with the exception of A-J1-6 which was prepared using Jacobia GAC as the precursor.

Lawerence Livermore National Laboratories (LLNL) provided 4 aerogel-GAC composite samples containing iron and/or manganese. Like GAC, the aerogel has very large surface area (approximately 1000 m^2/g), but it has the added advantage of being hydrophobic with a low density. Unlike GAC, the composite can remove both volatile organic compounds (VOCs) and metals. The composite consists of approximately 10% of a functionalized hydrophobic silica aerogel and 90% virgin coconut shell GAC. Aerogels are open foam like structures with high surface areas, low densities and high porosity. The composite materials are formed by mixing hydrophobic sol-gel precursors with chemical agents including those with iron and manganese functional groups, gelation catalysts, and GAC. After gelation of the sol-gel, the mixtures are supercritically dried to form aerogel-GAC composites.

Table 2.3 summarizes some of the characteristics of the aerogel-GAC composites. The pretreated GAC material with the higher iron content (294 and 295) removed the most arsenate. Without pretreatment (virgin GAC) the presence of manganese seemed important in aiding in arsenate removal (285 versus 291). The 285 GAC also had significantly more surface area than 291.

Fe-GAC samples from Solmetex Inc. and LLNL were crushed in a ceramic mortar and pestle and then sieved to 100x140 mesh size. This separation procedure of the media was conducted wet using nanopure water to wash the Fe-GAC material to prevent entrainment of fines. Most media provided to ASU from Clemson University and Solmetex had a moisture content within 30-40%; however some samples had moisture content out of this range. For this reason the experiment results were interpreted on a dry weight basis. Before performing each experiment the specific media to be used was tested for moisture content. Each time one gram of the sample was weighed in an analytical balance, and then placed in an aluminum weighing dish covered with aluminum foil. These samples then were placed in a Thermolyne 6000 oven at temperature of $100^{O}C$ for approximately 12 hours. After this step the samples were left to cool for one hour and then weighed again. This difference in weight was used to calculate the moisture content of the initial sample. This dry weight determination procedure was done in duplicate to assure its accuracy and then an average of the samples taken as the final value.

SPECTROSCOPIC CHARACTERIZATION

X-ray diffraction (XRD) analysis and X-ray photoelectron spectroscopy (XPS) analysis were performed on Fe-impregnated GAC samples for characterization of the materials. These iron-oxide impregnated GAC composites from Clemson University were modified thorough the duration of the experimental work as a means of changing structural properties to improve arsenic removal. The XPS and XRD tests were helped to measure the critical parameters of each different composite and were preformed after each modification. The instruments used were a scanning auger microprobe surface analysis system (XRA TOS XSAM 800) and a high resolution X-ray diffract meter (Micro photonics, Allenton, PA) equipped with Cu $K\alpha$ radiation (40KV, 25mA). Eight of the fourteen Fe-impregnated GAC samples provided by Clemson University were included: one virgin sample (C-1), one ion exchange treated sample (C-I3-4), two iron hydroxide precipitated samples (C-II4-11 and C-II14-2), two iron-deposited samples (C-III5A and C-III10A) and two zero-valent impregnated samples (C-IV6-8 and C-IV13-6).

XPS Analysis

XPS was employed to determine elemental surface composition of Fe-impregnated samples. Characterization results are summarized in Table 2.4. All samples contained oxygen (O1s), carbon (C1s), silicon (Si 2p), and iron (Fe2p3/2). Information for the surface characterization is limited for up to 5 nm depths from the external surface of the particle.

Iron content of the samples varied from 6 to 11%. Sample C-5A contained the highest amount of Fe, which is about 11%, followed by C-I3-4 (9.5%) and C-III10A (8.9%). All other samples contained similar amounts of iron (~6-7%). The silicon/silica content varied from 2-16%. Sample C-II4 contained the highest amount of silica (i.e., 16.5%), followed by C-III10A (i.e., 5%), C-II14 (i.e., 5%) and C-IV13 (i.e., 4.5%). All other samples contained similar amounts of silica (~2-4%).

Peaks for iron (i.e., Fe2p3/2) are detected at different binding energy levels depending upon the chemical form on the surface (e.g., elemental iron at 707eV, Fe(II) as FeO at 709.3eV, Fe(III) as Fe2O3 at 710.8eV, FeOOH at 711.5eV). As the iron peaks are weaker relative to carbon and oxygen peaks and become influenced by the background noise, any information obtained from XPS regarding the bonding structure of Fe has limited applicability.

XRD Analysis

The same eight samples mentioned in the XPS tests were also analyzed for X-ray diffraction pattern. Peaks of graphite, quartz, magnetite and elemental iron were observed in different samples. The width of the peaks suggests that samples are not purely crystalline but slightly amorphous. All samples have a peak at diffraction angle (2θ) of 26.6, which corresponds to the graphite crystalline structure of carbon. Silicon (i.e., 2θ - 20.85) as quartz was detected at all samples. Iron as a form of magnetite structure (i.e., 2θ - 34.4, 62.62) was noted in samples C-III10A, C-III5A, C-IV13, C-IV6 and C-II4, whereas iron in a range of different forms (i.e., 2θ - 44.35) was noted in C-I3, C-III10A, and C-III5A. Iron peaks were not noted in the virgin GAC sample or C-II14. As all samples were attached to a glass plate with gel before analysis, area coverage on the glass plates for C-II4 and C-II14 was not adequate due to non-sticky nature of the particle. All samples were 100x140 mesh, a smaller particle size is expected to provide better area coverage.

STOCK SOLUTION PREPARATION FOR EXPERIMENTS

All stock solutions used for batch experiments and column studies were prepared using reagent grade chemicals. Arsenate and arsenite stock solutions were prepared using Fisher Scientific reagent-grade arsenic acid ($Na_2HAsO_4 \bullet 7H_2O$) and sodium arsenite ($NaAsO_2$), respectively. 5mM of $NaHCO_3$ was used for pH buffering and nitric acid (JT Baker ultra pure reagent grade Ultrex II Nitric) to limit the pH within 7.0-7.5 units. MTBE and benzene were from Fisher Scientific. These stock solutions (small volumes ~3-4L) were mixed using a VWR Scientific standard 360 stirrer and magnetic stir bars. For column studies in which large volumes of water were needed, a Cole-Parmer Stir-Park mixer was used for mixing by placing this tool directly in the tank containers.

All glassware needed for the preparation of these solutions was cleaned prior to use in accordance with glassware cleaning procedures as described in the Analytical Methods section.

BATCH ARSENIC ADSORPTION EXPERIMENTS

Batch Kinetic Test Procedure

60-mL HDPE Nalgene bottles were used for batch experiments. 10-mg (dry weight) of Fe-GAC was added to each bottle. 40-mL of a pH buffered solutions containing arsenate were placed in the bottles. The samples were placed in a box and agitated to provide mixing. An orbital shaker (Barnstead/Thermolyne, model M49235) was used. Samples were sacrificed after 0, 1-hr, 6-hr, 1 day, 3 days, 7 days,14 days and 21 days. Fe-GAC media was separated by filtration using a Whatman 0.45 µm filter. Arsenic content in the filtrate was measured.

Batch Isotherm Test Procedure

Fixed masses of Fe-GAC were added to HDPE Nalgene bottles (250-mL, 1-L) containing the test solution with arsenic. The sample bottles were placed in a mechanical shaker at low speed for approximately seven days. Then the samples were filtered (0.45µm Whatman) to remove the Fe-GAC media. For experiments with arsenic, benzene and MTBE, 100-mL clear glass serum bottles (Fisher Scientific) with gas-tight lids were used.

Batch Isotherm Test using Modified NSFI-53 challenge water

Several batch tests were conducted to determine the water quality factors found in natural waters that affect arsenic removal by Fe-GAC media. A modified NSFI-53 challenge water was used to determine the significance of sulfate, fluoride, phosphate, bicarbonate and other ions (Table 2.5). The effects of silica concentrations (0 and 20 mg/L) and vanadium concentrations (0 and 100 µg/L) were also studied, separately, by preparing the NSFI-53 water with or without these metals. pH effect in arsenic removal was also tested (6.5, 8.5) at the same time with the parameters above mentioned. The procedure to make and use the NSFI-53 water is as follows:

1. Chemicals were added to nanopure water to meet the specific characteristics shown in Table 2.5.
2. Add sodium silicate ($Na_2SiO_3 \bullet 9H_2O$) to achieve a test tank concentration of 93 mg/L $Na_2SiO_3 \bullet 9H_2O$. Stir and transfer the solution to the test container.
3. Add sodium bicarbonate ($NaHCO_3$) to achieve a test concentration of 250 mg/L $NaHCO_3$. Stir and transfer to the test container.
4. Separately add magnesium sulfate ($MgSO_4 \bullet 7H_2O$), sodium nitrate ($NaNO_3$) and sodium fluoride (NaF) to achieve test concentrations of 128mg/L, 12mg/L and 2.2 mg/L, respectively.
5. Add sodium phosphate ($NaH_2PO_4 \bullet H_2O$) to achieve a test concentration of 0.18 mg/L $NaH_2PO_4 \bullet H_2O$. Stir and transfer to the test container.
6. Add calcium chloride ($CaCl_2$) to achieve a test concentration of 111mg/L $CaCl_2$. Stir and transfer to the test container.
7. Adjust the pH of the solution using HCl or NaOH to 6.5±0.25 for the low pH test and to pH 8.5±0.25 for the high pH test.
8. Add arsenic solution in the test container, depending on the desired concentration of arsenate in the water. For these experiments enough arsenic solution was added to reach a concentration of 100 µg/L of As(V).
9. Mix and measure the final pH and adjust as needed.
10. For vanadium tests, instead of adding sodium silicate in step 2, sodium vanadium (Na_3VO_4) is added to achieve 0.36 mg/L Na_3VO_4.

Sample Filtration Procedure

All samples from the batch experiments were filtered with a Gelman 25 mm filter holder and a 0.45 µm Nuclepore polycarbonate membrane filter (0.45 µm Whatman). A 60-mL BD syringe with plastic tubing was used to take the sample out of the bottle, and then the 60-mL water sample was passed through the filter to remove the adsorbent media and poured directly into a cleaned 60-mL HDPE Nalgene bottle or in cleaned glass 100-mL serum bottles in the case of organic samples. For every water sample the syringe was rinsed with nanopure water and a new 0.45µm Whatman filter loaded in the filter holder.

RAPID SMALL SCALE COLUMN TESTS

Rapid Small Scale Column Tests (RSSCTs) were developed in the 1980's to evaluate removal of organics by GAC in hydrodynamically-scaled laboratory columns based upon pilot- and full-scale operational parameters (GAC media size, loading rates, EBCT, etc.). This concept was extended for arsenic testing using porous metal oxide (Badruzzaman 2002). Scaling can be based either upon proportional (PD) or constant (CD) diffusivity assumptions (Table 2.6). For arsenic removal by porous metal oxides it was concluded that PD scaling was most appropriate (Badruzzaman 2002). Proportional diffusivity (PD) scaling equations were used for perchlorate removal on iron-preloaded GAC. It is believed that PD scaling is appropriate for arsenic (Westerhoff and Badruzzaman 2003; Westerhoff, De Haan et al. 2006). All RSSCTs employed herein will use PD scaling designs.

RSSCTs using Fe-GAC materials were sized with PD assumptions. Columns studies were performed with EBCT_{LC}'s of 2.5 minutes (samples C-II4, C-II9, C-IV13 and C-II14), 4 minutes (samples C-II4, C-III5, C-IV6, C-IV11, S-1, and S-3) or 10 minutes (samples S-1, S-2). Flow rate was set to approximately 11-mL/-min with a Reynolds-Schmidt number of 1000 for all of these experiments. A spreadsheet was designed (Table 2.7) based on the scaling equations presented above in which design parameters are calculated for small scale columns tests.

Small Scale Column Packing Procedure

Figure 2.1 shows the main components required for a column experiment and a schematic of a typical set up. The list of parts and procedure to pack a glass column is described as follows:

1. Material and Components:

- Small glass column with diameter of 1.1 cm and a length of 30 cm (Ace Glass)
- Inlet endcaps with filter ring and outlet endcaps with o-ring (Spectrum Chromatography)
- Glass wool
- 5 mm diameter-borosilicate glass beads (VWR)
- Teflon tubing of 3.2 mm diameter (Spectrum Chromatography)

- QG150 piston pumps (Fluid Metering Incorporated, FMI)

2. Sequence Procedure:

- A clean glass column with the outlet endcap is filled with nanopure water and glass wool added.
- 5 mm diameter glass beads are added to disperse the influent flow.
- Approximately 1 cm of glass wool is added at the top of glass beads to support the media.
- The Fe-GAC media (100x140 mesh) is added using nanopure water to flush the material down until reaching the required length or mass.
- After packing the media, it was backwashed to remove the fines at a low flow rate (~10-mL/min) in up flow mode with nanopure water until the effluent looked clear.
- Once the media is backwashed, 1 cm of glass wool is added followed by glass beads.
- The endcaps are connected to the Teflon tubing (inlets to the pumps and raw outlets to sample waste/collection points). It is critical to maintain the sample waste/collection tube elevation at an elevation above the inlet end-cap of the RSSCT column to prevent air bubbles from entering the packed bed.

The tank containers for the groundwater used for these column studies were HDPE reservoirs from Nalgene. The volumes of these containers were 50 and 150 gallons. All the tanks were cleaned with nanopure water several times prior to use.

Sampling Procedure and Flow Rate Setting for Rapid Small Scale Columns

All column studies were conducted in the water quality laboratory at ASU. The inlet and outlet tubing were 1/8th inch inside diameter Teflon tubing. Influent groundwater was stored and pumped to the RSSCTs from either a 50 or 150 gallon HDPE tanks. The pumps used in these experiments were QG150 piston pumps with Q2CSC pump heads purchased from Fluid Metering Incorporated (FMI). Water samples were collected directly from the outlet Teflon tubing line into 60-mL HDPE Nalgene bottles as required and then preserved with 0.15% nitric acid according to the procedures described in the Analytical Methods section. Samples collected for MTBE-benzene adsorption experiments were stored in clear glass 100-mL serum bottles for analysis and stored at 4°C.

The flow rate of the water thorough the columns was measured in a very simple procedure. Using a stopwatch and a 100-mL graduated cylinder from VWR the water from the outlet line was collected in the graduated cylinder for 3 minutes. Flow rate was measured and adjusted throughout the course of the RSSCT. However, the FMI piston pumps were found to be extremely stable and rarely needed flow adjustment during the course of an RSSCT experiment.

ANALYTICAL METHODS

Sample Preservation

Samples that were collected for trace metals analysis or for arsenic measurements were preserved with nitric acid (JT Baker ultra pure reagent grade Ultrex II Nitric). 0.15% total volume of nitric acid was added to the 250-mL and 60-mL sample bottles for a result of approximately 350 µL and 90 µL of acid, respectively. All samples acidified achieved a pH of around 2.0 units. Samples were stored in the dark at 4^{o}C until the time of analysis.

Glassware Cleaning Procedure

All glassware, bottles and glass RSSCT were rinsed with nanopure water before being submerged in a 0.1 % nitric acid bath for 24 hours prior to their use. Then equipment was immediately rinsed with nanopure water at least three times and allowed to air dry. Clean bottles were stored and placed in ziplock plastic bags before their use to prevent contamination.

Arsenic Analysis by Graphite Furnace Atomic Adsorption (GFAA)

The instrument used for arsenic analysis is a Varian SpectrAA 400 Zeeman graphite furnace atomic adsorption spectrometer equipped with correction capabilities (zeeman background). This particular instrument has an Arsenic super lamp with a photron boosted device. All water samples were dispensed into the furnace with the auto sampler device included in this instrument. All samples were acidified with nitric acid before analysis.

The instrument was calibrated using freshly prepared arsenic standards using an atomic spectral standard from VHG labs. The solution contains an arsenic concentration of 1000 µg/L and a matrix of 5% HNO_3 that was blended to reach the appropriate operating range for the instrument (2, 5, 10, 20, and 30 µg/L). 0.1% nitric acid was also added to the standards to reach the same characteristics of the water samples. The 1000 µg/L arsenic solution from VHG labs was blended to achieve a stock solution of 500 µg/L with 0.1% nitric acid. A five-point calibration curve was developed. All volumetric glassware used for the arsenic stock solution and the standards preparation was properly cleaned following the same procedure described in the Glassware Cleaning Procedure prior to use.

The Varian SpectrAA GFAA uses the analytical method 200.9 for trace elements; the method detection limit described and calculated in the Detection Limit Procedure was determined to be approximately 1 µg/L. However the actual detection limit and linear ranges are dependent on the sample matrix and instrumentation parameters selected for each operation. GFAA sensitivity and limited linear range generally implies the need to dilute the samples before every analysis. For this project all samples with concentrations within the range 50-250 µg/L were blended from 10 to 1 times, but most of the samples fell within the range of the standard curve calibration of 2-30 µg/L. For the sample dilution preparation, a stock of nanopure water solution with 0.1% nitric acid was made every time. An auto pipette was then used to dispense the required nanopure solution in the 2-mL disposable cups used for the samples analysis, the second step was to add (with a different clean pipette) the required amount of the water sample depending of the dilution factor. Then the total volume of the sample in the cup was mixed using the auto pipette to remove approximately one-third of the volume and then re-dispensed again into the cup several times to allow a complete and efficient dilution of the water sample. The procedure was repeated for each sample using clean pipettes every time.

Water samples were analyzed by GFAA with the use of a standard calibration curve with a range of 2-30μg/L. The calibration curve should show a linear response for accurate results when measuring trace metals in drinking water samples. Figure 2.2 shows the variability of the slope of the standards calibration curve from several GFAA analyses performed during 2005. An external Quality Control (QC) Check Standard was purchased from VHG Labs and prepared for an arsenic concentration of 10 μg/L following the proper instructions in order to compare and verify the accuracy of the calibration standards. This verification with the quality control sample was realized every nine samples through the complete analysis. In every analysis the standard deviation of these external quality control samples was calculated and the variation was always less than 10%. Figure 2.3 presents a summary of QC values obtained from several GFAA analyses performed during 2005. The variability of this sample fluctuated between 8 to 11 ppb.

The determination of the Method Detection Limit (MDL) was followed in accordance to the guidelines described in Appendix B of the Federal Register. Seven aliquots of the estimated MDL value were prepared at five times the desired detection limit, in this case of 1 μg/L. The MDL was determined to be 0.54 μg/L from the deviation standard of the seven replicates as shown in Table 2.8.

Gas Chromatography (GC) Analysis

Water samples were analyzed for organics removal by using headspace gas chromatography (GC) procedures. The GC instrument (SRI Model 8610C) was equipped with a 0.53mm ID x30m MXT-Vol glass capillary column with a 2.0 mm. 0.5-mL of headspace gas was injected into the GC instrument, which was set isothermally at 80°C for 2 -min in each sample.

Standards of MTBE and benzene were prepared in methanol. The density of MTBE (ρ_{MTBE} = 0.743 g/cm^3) or benzene ($\rho_{benzene}$ = 1.01 g/cm^3) were used to prepare 10,000 mg/L stock solutions in methanol. For example, 0.471-mL of MTBE was placed into 35-mL of methanol to prepare a 10,000 mg/l stock solution. Figures 2.4 and 2.5 present calibration curves.

Other Measurements

pH Measurement

For water samples required for temperature and pH measurements, a φ240 Beckman basic meter which includes a pH indicating electrode, an automatic temperature probe and a different range of pH buffers (1.68, 4.00, 7.00, 10.01, 12.45) was used. This instrument is equipped with selectable resolution, automatic temperature compensation (ATC), Auto-Find™ that automatically recognizes stored buffers, and Auto-Read™ to lock onto stable readings. The electrode and automatic temperature compensator probe were rinsed with deionized water and the excess blotted free using Kimwipes^{TM}. Then the electrodes were stirred briefly in the samples and the readings recorded. The same procedure was followed for each sample.

Conductivity Measurements

Conductivity measurements were done in the central laboratory using a conductivity meter (VWR model 2052-B) which uses a Pt-plated dip electrode. The instrument was standardized using a factory provided 718 μΩ standard solution. Measurements were made in a 20 mL test tube. Between each sample the dip electrode was rinsed with ultrapure water and dried with Kimwipes^{TM}.

Dissolved Organic Carbon (DOC) Analysis

Dissolved organic carbon (DOC) was analyzed with a Shimadzu TOC 5050A carbon analyzer, and UV absorbance of DOC at 254 nm (UVA254) was measured with a Shimadzu UV/Vis 1601 Spectrophotometer. For the UV absorbance analysis the wavelength was set to 254 nm. Optically cells were purchased from Fisher Scientific for the analysis; these cells were rinsed several times with ultrapure water before use. All samples expected to be over 1.0 absorbance were blended with ultrapure water prior to analysis. Specific absorbance (SUVA) was calculated as UVA254 divided by DOC. The MDL for DOC was 0.2 mg/L.

Table 2.1 Fe-GAC media properties provided by Clemson University

Iron Impregnation Approach	Sample ID	Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Micropore Volume (cm^3/g)	Micropore + Macropore Volume (cm^3/g)	pH_{ZPC}	Iron Content (mg Fe/g - GAC)
HD3000 GAC	C-1	686	0.712	0.266	0.446	5.3	< 3
HD Heat Treated	C-2	768	0.726	0.298	0.428	7	<3
HD Steam treated	C-7	853	0.790	0.325	0.465	7.4	<3
I. Ion exchange and heat treatment HDHTFeS	C-I3-4	778	0.724	0.295	0.429	6.8	36.2
	C-I8-4	860	0.766	0.334	0432	5.6	40.9
II.Iron hydroxide precipitation HDHTFeOH HDSTFeOHI	C-II4-11	646	0.649	0.249	0.400	6.8	116.3
	C-II4B-3	679	0.642	0.247	0.385	7.2	34.0
	C-II9-8	762	0.726	0.296	0.430	6.9	78.8
	C-II14-2	832	0.752	0.321	0.431	7.5	20.9
III.Organic comp to deposit iron HDHTFeOX	C-III5-16	619	0.587	0.231	0.356	6.5	163.5
	C-III10-9	772	0.690	0.301	0.389	6.1	87.3
IV.Zero valent iron surface HDHTFe^0 HDST,16NO, Fe2A	C-IV6-8	653	0.696	0.241	0.455	6.3	83.3
	C-IV11-7	742	0.704	0.288	0.416	6.6	74.3
	C-IV13-6	788	0.728	0.302	0.426	8.5	58
	C-16-3	836	0.783	0.31	0.473	5.4	31.6
	C-17-3	863	0.781	0.325	0.456	5.5	30.9

Table 2.2 Fe-GAC media properties produced by Solmetex and ASU

Supplier	Carbon Type	Sample ID	Iron content (mgFe/g-GAC)
Solmetex Inc.	Norit HD3000	S-1	67.6
	Norit HD3000	S-2	38.4
	Norit HD3000	S-2B	112
	Norit HD3000	S-4	105
ASU (Solmetex Fe-Treatment)	Norit HD3000	A-3	71.8
	Jacobi GAC	A-J1	63

Table 2.3 Characteristics of aerogel-GAC composites

Aerogel-GAC composite ID	Iron content (%)	Manganese Content (%)	Granular Activated Carbon	Surface Area (m^2/g)
Virgin GAC	0	0	Coconut shell	--
L-285	0.8	0.02	Virgin coconut shell	739±20
L-291	0.8	0	Virgin coconut shell	450±11
L-294	0.75	0	Pretreated	--
L-295	0.96	0	Pretreated	--
L-265	0.61	1.2	Pretreated	853±23
L293-2	0.15	0	Virgin coconut shell	--

Table 2.4 Elemental surface composition of samples

Sample ID	O (%)*	C (%)	Si (%)	Fe (%)
C-1	33.63	58.96	4.03	0.0
C-I3-4	39.24	50.1	2.62	6.93
C-II4-11	19.68	55.33	16.51	6.78
C-II14	23.78	61.93	5.09	6.5
C-III5A	29.9	53.71	2.77	11.05
C-III10A	27.97	55.54	5.09	8.86
C-IV6	31.11	55.7	2.69	7.56
C-IV13	23.73	53.97	4.57	9.54

* Atomic percent basis

Table 2.5 NSFI-53 challenge water formulation

Parameter	Target Value
Mg^{+2}	12 mg/L
SO_4^{-2}	50 mg/L
NO_3^{-1}-N	2.0 mg/L
F^{-1}	1 mg/L
SiO_2 or Na_3VO_4	0 & 20 mg/L 0 & 100 µg/L
PO_4^{-3}-P	0.04 mg/L
Ca^{+2}	40 mg/L
As(V)	100 µg/L
Temperature	$20^oC \pm 2.5^oC$
Turbidity	< 1 NTU
pH	6.5±0.25 or 8.5±0.25

Table 2.6 RSSCT scaling equations

Scaling Assumption	CD or PD Specific Relationships	General Relationships
Constant Diffusivity (CD: X=0)	$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{d_{p,SC}}{d_{p,LC}}\right]^{2-X} = \frac{t_{SC}}{t_{LC}}$ Eqn 2.1	
	$\frac{V_{SC}}{V_{LC}} = \left[\frac{d_{p,SC}}{d_{p,LC}}\right]$ Eqn 2.2	$\frac{V_{SC}}{V_{LC}} = \left[\frac{d_{p,SC}}{d_{p,LC}}\right] \times \frac{\mathrm{Re}_{SC} \times Sc}{\mathrm{Re}_{LC} \times Sc}$ Eqn 2.5
Proportional Diffusivity (PD; X=1)	$\frac{D_{SC}}{D_{LC}} = \left[\frac{d_{p,SC}}{d_{p,LC}}\right]^{X}$ Eqn 2.3	$\mathrm{Re} = \frac{V \times \rho_L \times d_p}{\mu}$ Eqn 2.6
	$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{d_{p,SC}}{d_{p,LC}}\right] = \frac{t_{SC}}{t_{LC}}$ Eqn 2.4	$Sc = \frac{\mu}{D_L \times \rho_L}$ Eqn 2.7

Table 2.7 RSSCT design parameters for simulating a 4 minute full-scale pilot system

Design Parameters	Simulated Pilot Scale	RSSCT (PD)
Input Parameters		
Particle radius (cm)	0.0513	0.0064
Column diameter (cm)	30.48	1.10
Column area (cm^2)	729.29	0.9499
Wet density (g/mL)	1.79	1.40
EBCT (min)	4.00	0.50
Loading rate (m/h)	10.11	7.03
Loading rate (cm/min)	16.85	11.72
BV to be processed	30000.00	30000.00
Flow rate (gpm)	3.25	
Flow rate (gpm/ft^2)	4.14	
Re*Sc (200,000-200)		1000.00
U (Pa s)	8.94E-04	0.00
P (kg/m^3)	1000	1000.00
Dl (Free liquid Diffusivity) (m^2/s)	1.00E-09	0.00
d (m)	0.001026	0.00
v (m/s)	0.002807	0.00
e (porosity)	0.25	0.25
Re	1.29E+01	1.12
Sc	893.7	893.70
Re*Sc	11522.10	1000.00
Design Data		
Flow rate (mL/min)	12285	11.13
Volume of media (mL)	49140	5.6
Length of the column (cm)	85.34	5.8
Mass of the media (g)	87960.6	7.8
Water required (L)	1474200	166.6
Water required (gals)	390000	44.1
Duration of experiment (days)	83.33	10.4

Table 2.8 MDL for GFAA analysis

Sample Type	Concentration (5.0 ppb)
Replicate 1	5.4
Replicate 2	5.5
Replicate 3	5.1
Replicate 4	5.0
Replicate 5	5.2
Replicate 6	5.3
Replicate 7	5.3
Mean	5.25
Std Deviation	0.1718
MDL	0.54

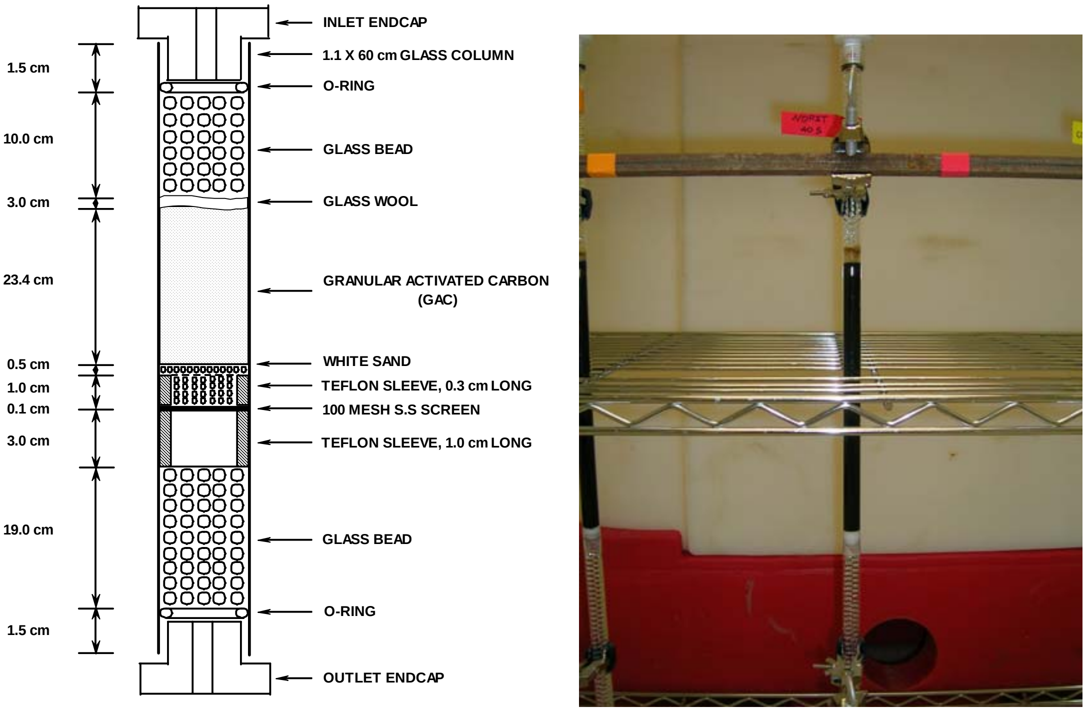


Figure 2.1 Schematic of a typical set up for a column study

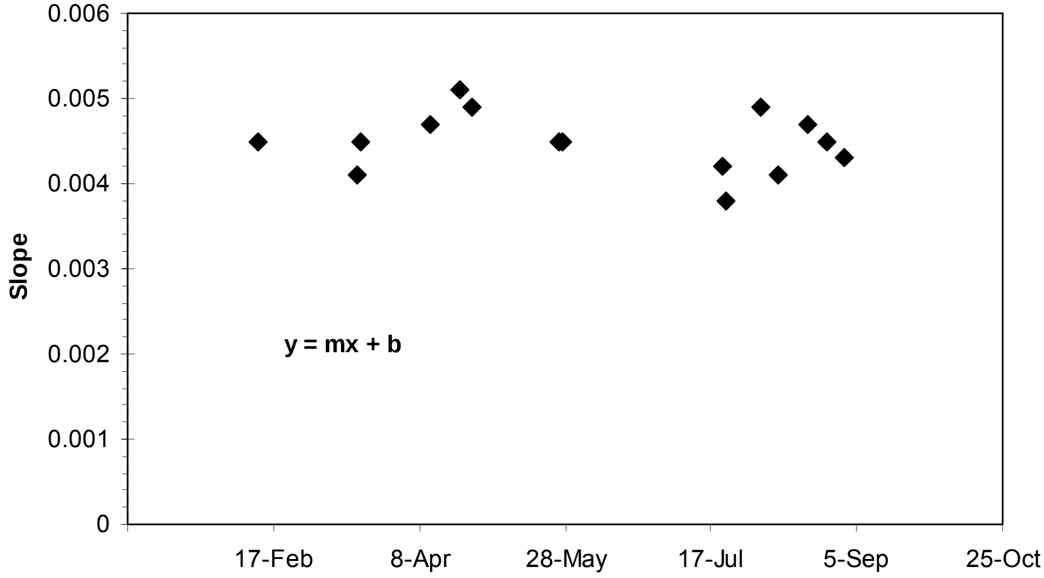


Figure 2.2 Variability of slopes of standard calibration curves for arsenic analysis by GFAA during 2005

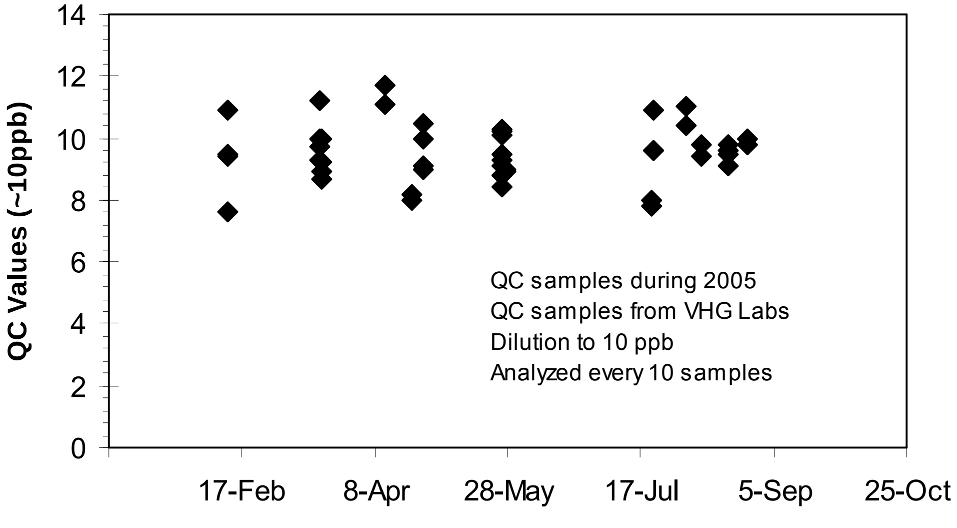


Figure 2.3 Summary of QC results for GFAA analysis during 2005

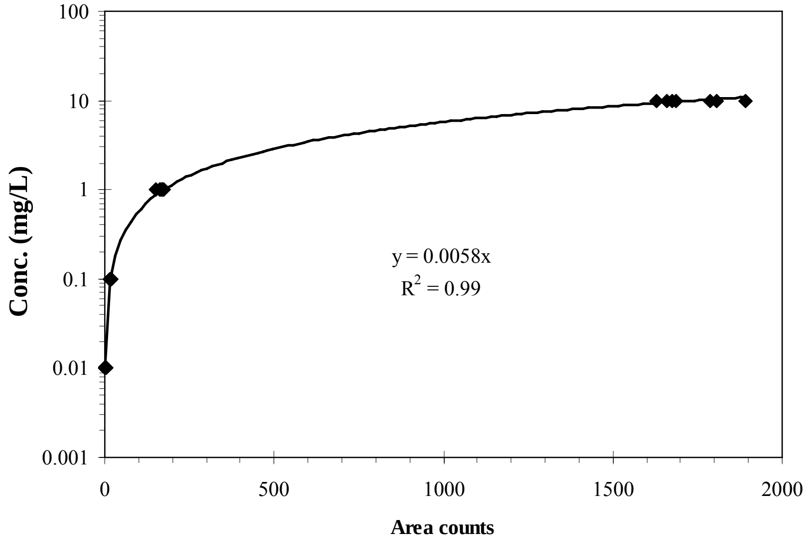


Figure 2.4 Standards calibration curve for MTBE

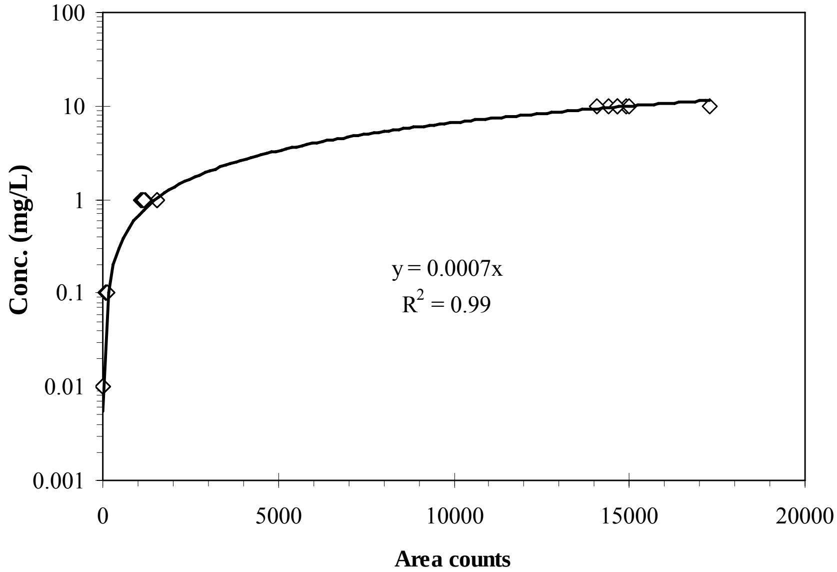


Figure 2.5 Standards calibration curve for benzene

CHAPTER 3 BATCH EXPERIMENT RESULTS

KINETIC TESTS

Most of the kinetic experiments were conducted using Clemson University samples with consistent 100x140 mesh size. Nanopure water, pH = 7.00 controlled with 5 mM of $NaHCO_3$ and spiked with As(V) concentrations of 100 µg/L was used. Adsorbent dosages of 0.25 g dry/L were set for each Fe-GAC sample (Figure 3.1). Samples C-2, C-II4-11, C-I8-4, C-III10-9 and C-IV11-7 were selected for kinetic experiments. Each composite represents a different iron deposition process for its impregnation (Table 2.1). C-II4-11 and C-IV11-7 had the highest adsorption capacity. Kinetic tests were conducted also to determine if some samples had lower capacity, but improved kinetics. However in all cases arsenic adsorption appeared to reach pseudo-equilibrium in approximately 3 days.

For comparison against existing commercial media, kinetic tests were conducted with granular ferric hydroxide (GFH) which is a commercial non GAC based pure iron (hydr) oxide media. From previous work, it was known that lower GFH dosages than Fe-GAC composites would be required to show any observable kinetics. Therefore a GFH dosage approximately 25 % less than that from Fe-GAC was tested (Figure 3.2). Additional tests show that GFH does not reach equilibrium until 20 to 30 days (Badruzzaman, Westerhoff et al. 2004). For the same mesh size GFH has a higher adsorption capacity than Fe-GAC samples tested, but the Fe-GAC appeared to have faster adsorption kinetics.

SCREENING TESTS

Clemson University Media

Batch screening experiments testing different Fe-GAC media (100x140 mesh size) were conducted in nanopure systems, pH = 7.00 buffered with 5 mM of $NaHCO_3$ with an initial arsenic concentrations of 100 µg/L (Figure 3.3). The contact time was set at 7 days based on previous experience. Subsequent kinetic tests verified that this duration was sufficient to reach equilibrium. Fe-GAC dosage of 0.25 mg dry/L was used. Samples C-II4-11, C-IV13-6, C-II9-8, C-II14-2, C-IV6-8 and C-IV11-7 removed ~75% of the initial As(V). A second batch screening test was conducted partway through the study as Clemson University produced three new Fe-GACs (C-16A-3, C-17A-3 and C-IV13B-6). These new media were designed based upon the results of characteristics of C-II4-11 and C-IV13. During these tests a subset of Fe-GACs from the first screening were used as a reference. Figure 3.4 shows that these new adsorbents had similar kinetic performance, although the initial C-II4-11 and C-II9-8 samples had higher adsorption capacity.

Arsenite

Screening tests were conducted for As(III) removal using selected Fe-GAC composites. Experimental conditions mirrored those for arsenate screening tests. Results are shown in Figure 3.5. C-IV13B-6 (zero valent iron) was slightly better than C-II4-11 (iron hydroxide precipitation). C-17A, C-16A and C-II4B-3 (all three treated by iron hydroxide precipitation) had similar performance for arsenite removal.

Solmetex Fe-GAC Media

Two samples of Solmetex Fe-GAC were provided, with and without acid pretreatment, these samples were manufactured using Norit HD3000. The non-acidified Solmetex Fe-GAC (S-1-7) contained 6.7% iron by dry weight (67.6 mgFe/g dry composite), and the acid-treated Solmetex Fe-GAC (S-2-4) contained only 3.8% iron (38.4 mgFe/g dry composite). This range of iron content is on the lower end of the materials provided by Clemson University that contained 6% to 13% iron by weight.

Batch tests were conducted with Solmetex Fe-GAC composites and the base GAC material (virgin HD3000 carbon). Figure 3.6 shows the results. Virgin HD3000 had no As(V) removal. The two Solmetex Fe-GAC composites had significant As(V) removal. S-1-7 and S-2-4 had similar performance despite the difference in iron content. The Solmetex Fe-GAC composites removed more (~90% for 250 mg/L of media) arsenic from the solution than the aerogel material (~45% removal), that was based upon Carbon Activated Corporations coconut-shell based GAC.

LLNL Fe-GAC Media

Sample L-294-1 is an iron functionalized hydrophobic silica aerogel composite provided by Lawrence Livermore National Laboratories (LLNL). The composite consists of approximately 10% silica aerogel and 90% virgin coconut shell GAC. This composite was tested in parallel with Fe-GAC media from Solmetex (Figure 3.6). L-294-1 adsorbed less arsenic(~45% removal) than S-1-7 and S-2-4.

Based upon adsorption experiments conducted in the past, aerogel L-294-1 sample was selected to perform new isotherm tests in parallel with the C-II4-11 composite from Clemson University. A nanopure system spiked with 100 ppb of arsenate and pH of 7.00 was used. The aerogel sample from LLNL was used in full mesh size due to a limited volume of the media for reducing it to 100x140 size; the Fe-GAC sample from Clemson University was used in 100x140 mesh size, no full size particle media was available. Doses were on the range of 50-2000 mg dry/L and 50-500 mg dry/L for LLNL and Clemson University composites respectively. Freundlich adsorption isotherm model ($q = KC_e^{1/n}$) was used to fit the results obtained. Good ($R^2 > 0.94$) isotherm fits were observed for both composites. C-II4B-3 appears as the stronger adsorbent for arsenate with a significant difference to the aerogel L-294-1 media, K values were 0.01 and 0.09 for LLNL (1/n=0.51) and Clemson University (1/n=0.80) samples, respectively, indicating the latter as the one with higher adsorption capacity for arsenic. The large difference in adsorption efficiency between these media may be attributed to the larger particle size of the aerogel sample due to pore blockage or bad distribution of the silica gel into the GAC material.

Previous work at LLNL has investigated uranium removal by a phosphorous enriched hydrophobic aerogel/GAC composite. Producing a P-enriched aerogel-GAC composite improved uranium removal above the GAC without the composite. Varying the type and amount of phosphorous (1% or 17% H_3PO_4) affected uranium removal, based upon analysis of isotherm data. Additional absorbance was confirmed via column tests and a field demonstration. This uranium-related work will be briefly discussed to demonstrate the potential for aerogel-GAC composite materials to remove oxo-anions.

More tests were conducted for arsenic and uranium removal using aerogel-GACs. Nanopure water with pH of 7.0 (5 mM $NaHCO_3$) spiked with 100 ppb of arsenate and 50 ppb of uranium (Aldrich standard solution) was used. The particle size of the media was 10x60 (due to lack of enough mass of the media this sample was not sieved to 100x140 mesh). Doses used were within the range of 50 to 2000 mg dry/L. A phosphate functionalized hydrophobic silica aerogel-GAC (sample L-05) and an iron functionalized aerogel (sample L-06) were selected for these experiments; L-05 contained 17% H_3PO_4. Both composites adsorb uranium from the solution, when equilibrium is reached 70% of U was removed. Sample L-05 had better potential for removing the contaminant and faster kinetics. This sample removed approximately 80% of arsenate in the solution which is comparable with other Fe-GAC materials from Clemson University. The better adsorption capacity of L-06 than L-05 might be explained by better impregnation of iron on the GAC particles or the poor distribution of silica aerogel on the composite, as visually observed by “patch” coverage of the Fe-GAC with whitish aerogel.

ISOTHERMS IN MODEL SOLUTIONS AND NATURAL WATERS

Model Solutions

Isotherm experiments were conducted for most Fe-GAC composites for arsenate removal based on screening and kinetic tests. Nanopure water with an arsenic concentration of 100 μg/L and 5 mM $NaHCO_3$ was used; the solution pH was regulated to 7.00±0.2. Media doses (100x140 mesh sizes) varied between 10 mg/L to 500 mg/L dry weight. 7-day contact times were used.

Clemson University Fe-GAC Media

Initially C-II4-11, C-II9-8, C-IV13-6 and C-II14-2 were tested and the results are presented in Figure 3.7. Figure 3.8 is a plot of the same adsorption data from which Freundlich Isotherm parameters were obtained. C-II4-11 and C-II9-8 performed better than C-IV13-6 and C-II14-2. This data is consistent with the pattern observed from screening tests.

Solmetex Fe-GAC media

S-1-7 and S-2-4 performed very similar in batch screening experiments with model solutions. Sample S-1-7 was selected for an isotherm test along with sample C-II4-11 from Clemson University and ArsenXnp media (Figure 3.9). ArsenXnp is currently a commercial hybrid ion exchange media from Solmetex which has an iron content of approximately 20%. ArsenXnp had a higher adsorption capacity than the rest of the samples. S-1-7 (which is 6.7% iron by dry weight) had a slightly higher capacity than C-II4-11 (11% iron content).

Two more Fe-GAC samples were produced by Solmetex and tested in isotherm experiments. These composites were prepared using virgin Calgon GAC instead of Norit HD3000. S-2B-11 and S-4-11 have 11.2% and 10.5% iron, respectively. C-II4-11 sample was included in this experiment for direct comparison of these media as arsenic adsorbents. Figure 3.10 shows similar performance between samples S-2B-11 and S-4-11. C-II4-11 had slightly lower capacity for arsenic adsorption (see also Figure 3.11).

ASU produced Fe-GAC composites following Solmetex iron deposition procedures. This process is similar to the one used in impregnating nano-iron onto ion exchange media (ArsenXnp media). ASU used virgin Norit HD3000 and Jacobi GAC as base material to produce samples A-3-7 and A-J1-6, respectively. A-3-7 and A-J1-6 contain 7% and 6% Fe, respectively. Figure 3.12 shows an isotherm in a model solution comparing both composites from ASU with S-4-11. The graph indicates that S-4-11 has slightly higher arsenic adsorption capacity. A-3-7 and A-J1-6 performed in a similar trend as the sample from Solmetex but with lower potential for arsenic removal.

Groundwaters

Isotherms were conducted in groundwater collected from Scottsdale, AZ 4E well site to test the effectiveness of the Fe-GAC composites when competing with other constituents found in natural waters. Scottsdale groundwater had an arsenic concentration of approximately 33 µg/L, TDS of 800 mg/L (conductivity ~1.18 mS) and silica concentrations of around 25 ppm. The pH of the water was lowered from 8.7 to 7.8±0.2. Media doses varied between 25-500 mg dry/L 100x140 mesh sizes. Contact time for these experiments was 7 days.

Arsenic adsorption was significantly lower than expected from the isotherm with C-II4B-3 in nanopure water as shown in Figure 3.13, suggesting that competing ions present in the water affected the performance of the Fe-GAC composite. The difference in pH (7.0 and 7.8) may also affect the capacity of the media for arsenic removal. Although these experiments were conducted at different initial As(V) concentrations, had no ion competition occurred the percentage removals should not have differed by the observed amount. Likewise, the slight pH difference between the tests should not have affected As(V) removal by the observed amount.

Figure 3.14 shows isotherms for As(V) on Solmetex samples in two dilutions of a local groundwater which has a TDS of ~800 mg/L (conductance = 1.18 mS). For these batch experiments S-1-7 and S-2-4 were combined in order to yield enough material for subsequent RSSCTs. The local groundwater was blended with DI water to evaluate the effect of naturally occurring competitive ions on As(V) removal. As(V) was maintained at a similar level in the experiments (~28 ppb) by spiking sodium arsenate. The adsorbent appears quite sensitive to the presence of naturally occurring ions, with lower adsorption capacity in the presence of a higher content of groundwater and its competing ions.

pH Effects

pH effects on performance of Fe-GAC composites for arsenate removal were tested with isotherm experiments. Model solutions (5 mM $NaHCO_3$; 100 µg/L As(V)) at pH of 5 to 9 were used. Media doses varied between 10-250 mg dry/L using 100x140 mesh sizes for a contact time period of 8 days (7-days would have been used, but it feel on a holiday). Fe-GAC composites from Clemson University were selected for this particular experiment due to performance in past adsorption experiments.

Figure 3.15 shows similar trends of adsorption efficiency of Clemson University composites as observed in past isotherm experiments (Figure 3.8). C-II4B-3 has slight better adsorption capacity for arsenate at pH of 5. The effect of pH on As(V) adsorption is observed clearly in Figure 3.16 in which the adsorbent performs better at pH levels of 5.0 and 6.5. Arsenic removal decreased at increasing pH values.

Silicate (Si) and Vanadate (V) Effects

To quantify the effect of pH and competing ions (hydroxide, silica, vanadium) batch experiments were conducted with C-II4-11. Effects of pH and silica (270 g/L $NaOHSiO_2$ Aldrich solution) were evaluated using a modified NSFI-53 challenge water matrix containing different ion concentrations (Table 3.4 in Experimental Methods). The results of adsorption tests using C-II4-11 are presented in Figure 3.17. As(V) adsorption was greater at pH 6.5 compared to pH 8.5. At pH 6.5 the addition of 20 ppm SiO_2 decreased As(V) adsorption by 25%, and by 80% at pH 8.5.

Effects of pH and vanadium were similarly evaluated using the same NSFI-53 challenge water matrix as above, but containing Na_3VO_4; no silica was added during vanadium experiments. Figure 3.18 demonstrates that 100 µg/L of vanadium decreases As(V) adsorption by less than 10%. If higher vanadium concentrations were used a greater competition may have been observed, but it was decided to evaluate a As(V) to V ratio that is common in western USA groundwaters.

CO-ADSORPTION OF ORGANIC CHEMICALS AND ARSENIC

Surface water from Rooselvelt Lake, AZ was used for the performance testing of Fe-GAC composites performance on As(V) removal when organics are present in the solution. C-II4B-3 and virgin Norit HD3000 (100x140 mesh size) were used for this batch isotherm experiment. Natural water was spiked with 100µg/L As(V) and pH adjusted to 7.00 with HNO_3. Results show that C-II4B-3 efficiently removed As(V) while no arsenic adsorption capacity was observed for virgin media in the surface water (Figure 3.19). Compared with previous experiments in model solutions the adsorption capacity of C-II4B-3 was 15 to 20 % lower in the surface water, again due to competing ions.

Comparing Rooselvelt Lake water to Scottsdale 4E well site groundwater, C-II4B-3 had less capacity (~20 %) for arsenic removal when tested in the groundwater (Figure 3.20). Figure 3.21 shows that both media removed similar amounts of dissolved organic carbon (DOC).

Several Fe-GAC composites were evaluated with Scottsdale groundwater spiked with arsenate, MTBE, and benzene. The results are illustrated in Figure 3.22 and Figure 3.23. Both Fe-GAC composites removed arsenate and the synthetic organic chemicals (SOCs). Because of its higher octanol-water partition coefficient, benzene adsorption capacity was significantly greater than MTBE adsorption capacity.

A-3-7 had a higher capacity for As(V) than C-II4B-11 (Figure 3.23). A-3-7 from ASU contains ~7% iron by weight. Both Clemson University and ASU materials were modified from the same base carbon material (Norit HD3000) and as a result had similar adsorption of the SOCs. This work shows that modifying GAC with iron does not impair the ability of the composite to continue to remove SOCs, while also removing arsenic.

SUMMARY

- Kinetic results showed that samples C-2, C-II4-11, C-I8-4, C-III10-9 and C-IV11-7 reached pseudo-equilibrium at approximately 7 days of contact time.
- GFH which is a commercial pure iron (hydr) oxide media was tested in parallel with the Fe-GACs and had higher adsorption capacity, but the Fe-GAC appeared to have faster adsorption kinetics.
- Screening test results for arsenate show that C-II4-11 and C-II9-8 had higher adsorption capacity (80% As(V)removal) than the rest of the Fe-GACs.
- In arsenite-based screening tests C-IV13B-6 had slightly better adsorption capacity than C-II4-11.
- Screening tests using S-1-7 and S-2-4 media had higher adsorption capacity for arsenic (90% As(V) removal) than L-294-1 and virgin Norit GAC samples.
- Initial batch isotherms on a model solution shows that C-II4-11 and C-II9-8 performed better than C-IV13B-6 and C-II14-2. This data is consistent with the pattern observed from screening tests.
- S-1-7 and C-II4-11 were tested in parallel with ArsenXnp (a Solmetex Inc. hybrid ion exchange product with a 20% dry weight iron content). ArsenXnp had much greater adsorption capacity than the other two. S-1-7 had higher adsorption capacity than C-II4-11.
- Two Fe-GACs from ASU along with S-4-11 were used for batch isotherms. S-4-11 (K value of 0.29) has slightly higher arsenic adsorption capacity. A-3-7 (K value of 0.18) has higher adsorption capacity than A-J1-6 (K= 0.13).
- An adsorption test in Scottsdale groundwater with C-II4-11 shows that this media's performance for arsenic removal is significantly reduced when competing with other ions. pH variations between 7.0 to 7.8 also affected the adsorption capacity of the media.

- Experiments at different pHs show similar trends of adsorption efficiency of Clemson University composites as observed in past isotherms. C-II4-11 has slightly better adsorption capacity for arsenate at pH of 5 than the rest of Fe-GACs. Arsenic removal decreased at increasing pH values.
- For evaluation of vanadate and silicate influence, C-II4-11 was tested. As(V) adsorption was greater at pH 6.5 compared to pH 8.5 with no silica. At pH 6.5 the addition of 20 ppm SiO_2 decreased As(V) adsorption by 25%. At pH 8.5 As(V) adsorption was diminished by 80%.
- Vanadate concentrations of 100 μg/L decreased As(V) adsorption by less than 10%.
- When testing in a surface water (Roosevelt Lake, AZ), C-II4B-3 removed As(V), while no As(V) removal was observed for virgin GAC-media. However, the arsenic adsorption capacity by C-II4B-3 was 15 to 20 % lower in the surface water than in model solutions, probably due to competing ions. K values were 0.13, 0.09 and 0.006$(\mu g/mg)/(\mu g/L)^{1/N}$ for C-II4B-3 when testing in nanopure, surface and groundwaters, respectively.
- C-II4B-3 and virgin media removed DOC similarly in surface water.
- Batch adsorption tests with arsenate, MTBE and benzene in Scottsdale, AZ groundwater (33%) demonstrated that both A-3-7 and C-II4B-3 remove arsenate and SOCs. Benzene had more affinity to both Fe-GACs than MTBE.
- A-3-7 had a higher capacity for As(V) removal than C-II4B-3. This work shows that modifying GAC with iron does not impair the ability of the composite to continue to remove SOCs, while also removing arsenic by the added iron.

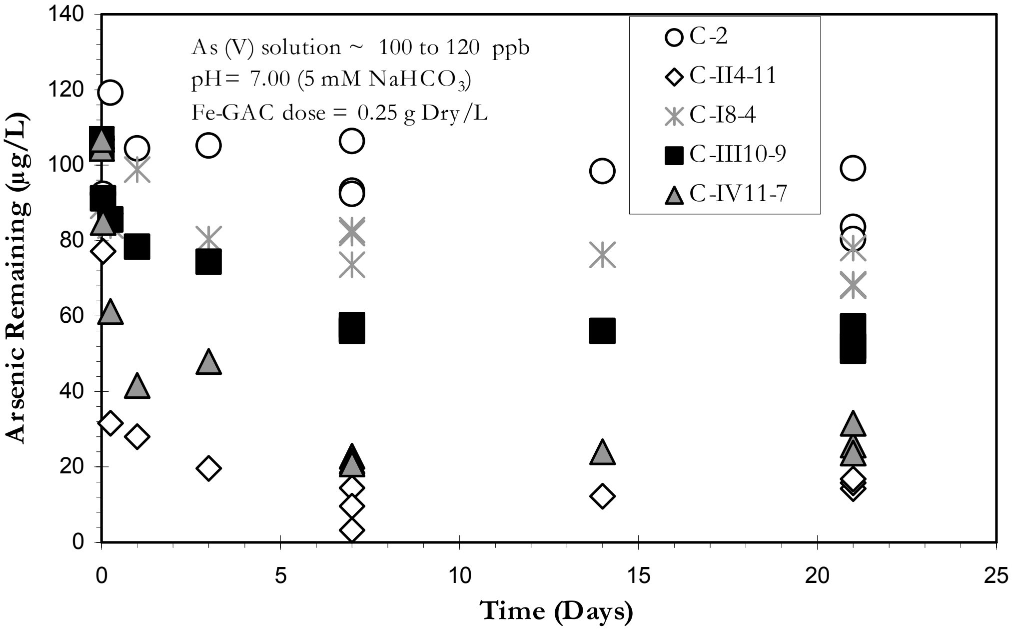


Figure 3.1 Kinetic tests using different Fe-GAC composites. Each composite represents a different approach for production

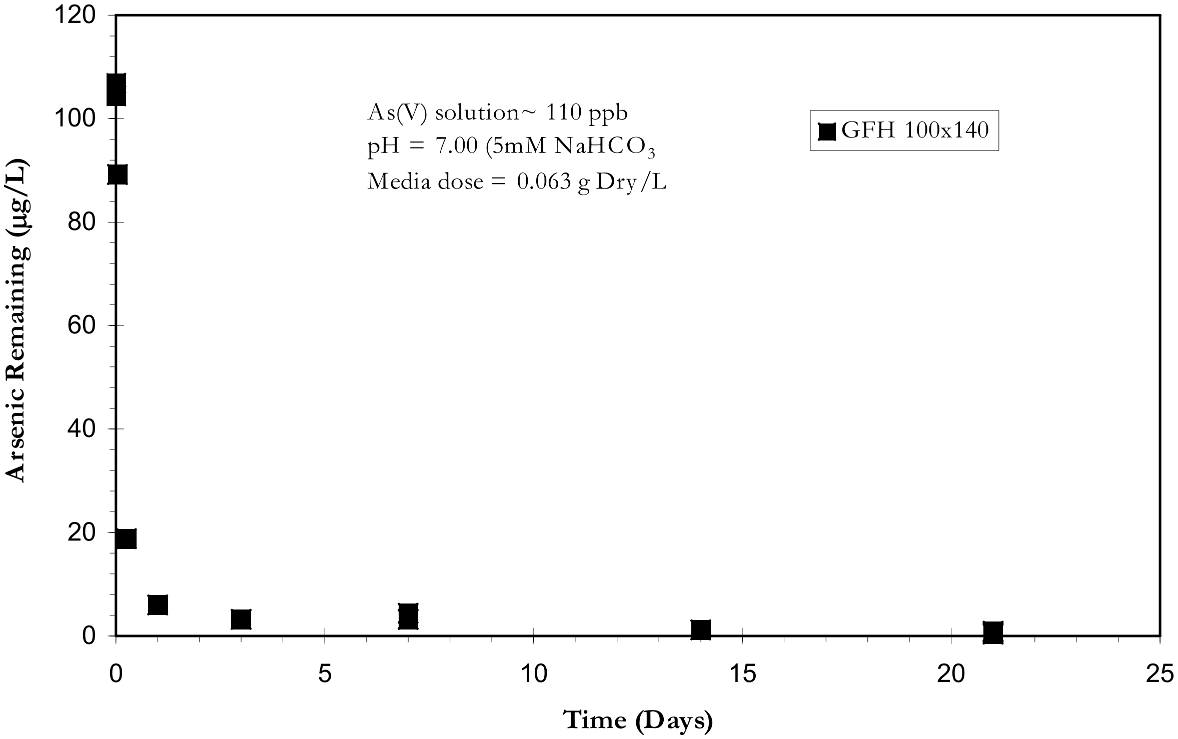


Figure 3.2 Kinetic tests with granular ferric hydroxide (GFH) at lower dosage than Fe-GAC tests

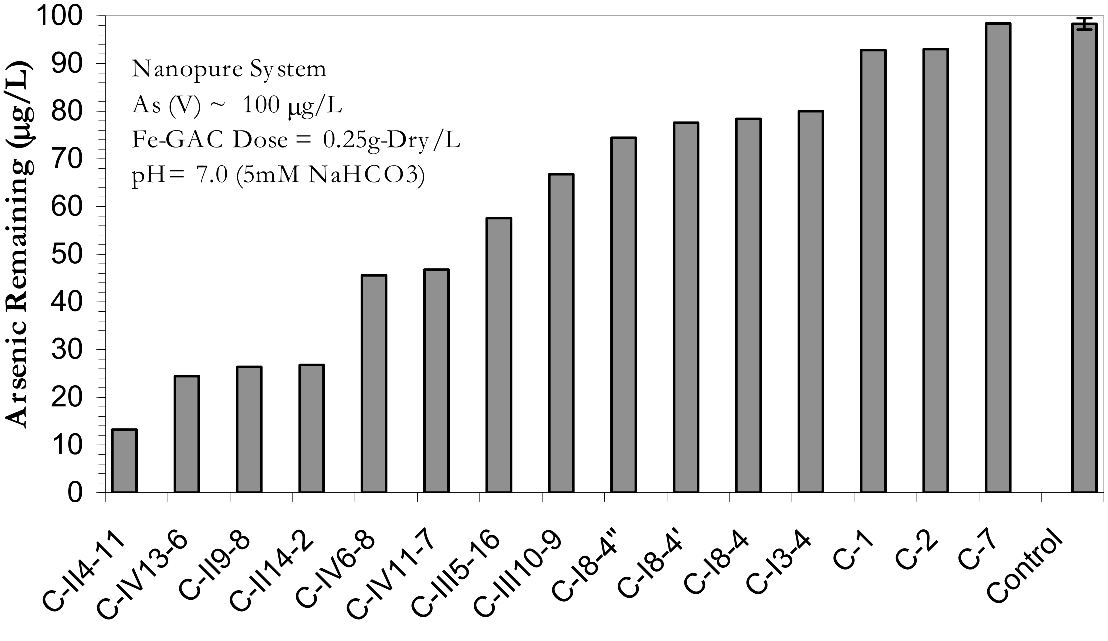


Figure 3.3 Batch Screening of Clemson University Fe-GAC samples (Oct-04). Control sample contained no Fe-GAC adsorbent

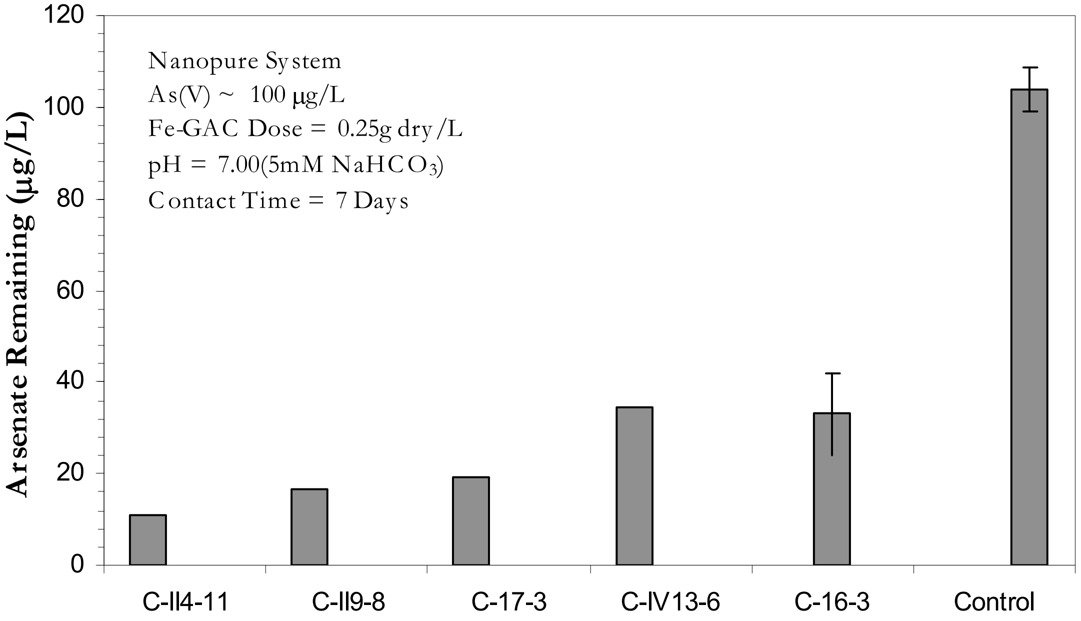


Figure 3.4 Batch screening of Fe-GAC samples from Clemson University (Jan-05). Sample 16A was tested in triplicate along with controls

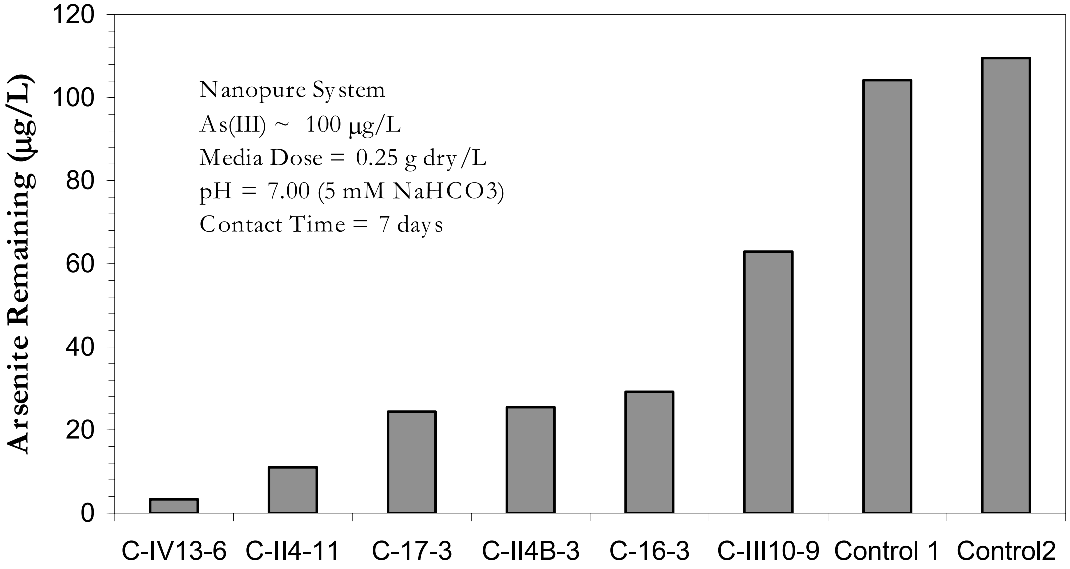


Figure 3.5 Screening test for As(III) removal using Fe-GAC samples from Clemson University (July-05). Control samples were tested in duplicate with no adsorbent

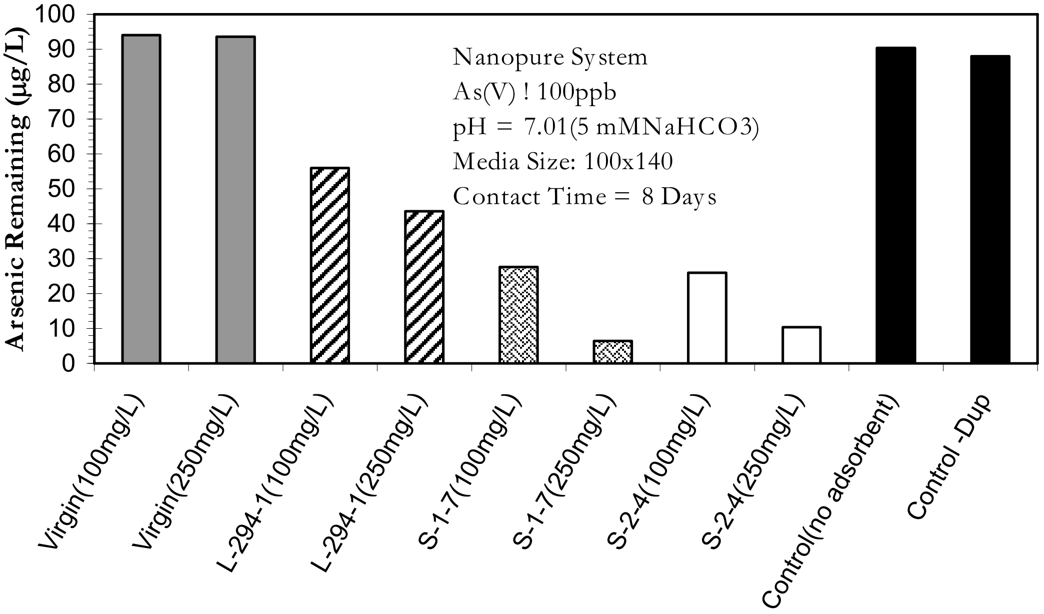


Figure 3.6 Batch adsorption test with virgin HD3000, LLNL aerogel 294 and two Solmetex Fe-GAC composites in Nanopure water system. Values in parenthesis are adsorbent dosages.

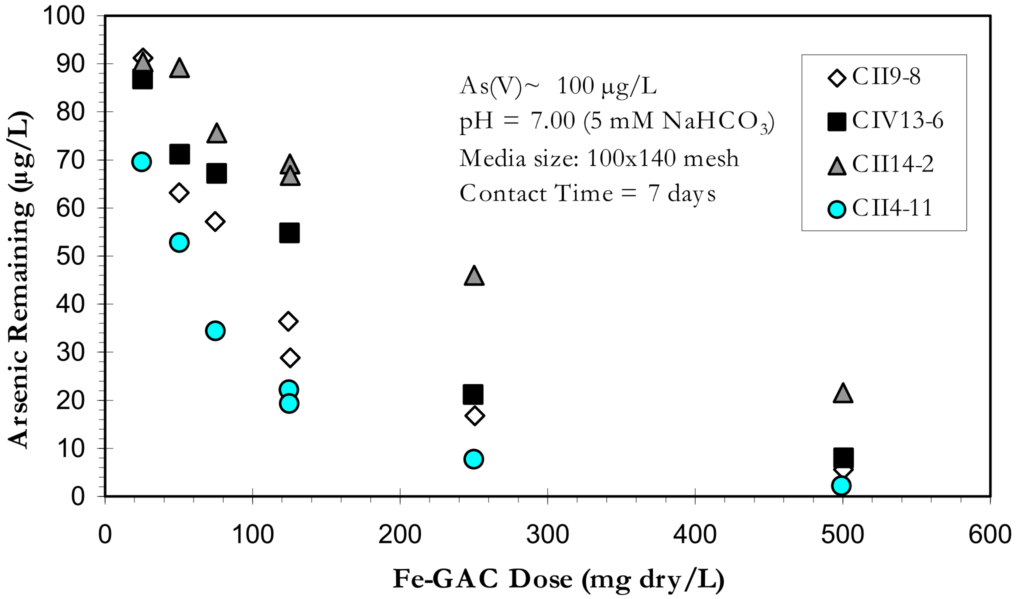


Figure 3.7 Adsorption test with different Fe-GAC materials from Clemson University. Jan-05

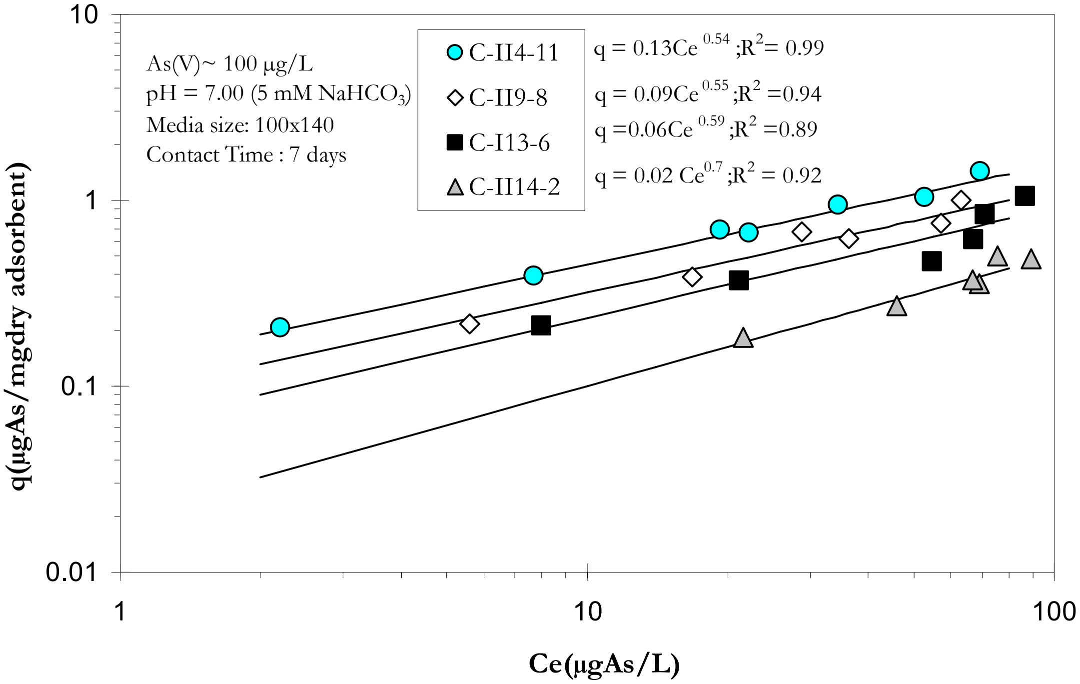


Figure 3.8 Log form of Freundlich adsorption isotherm with different Fe-GAC materials from Clemson University. Jan-05

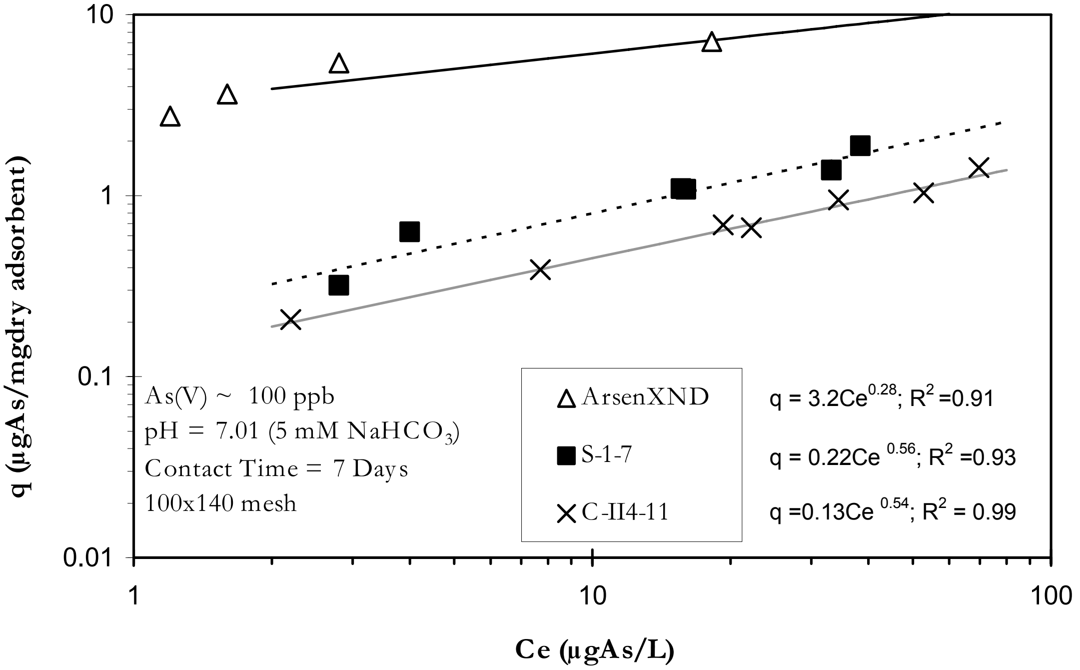


Figure 3.9 Isotherm test in model solution comparing different Fe-GAC media from Solmetex and Clemson University. March 2005

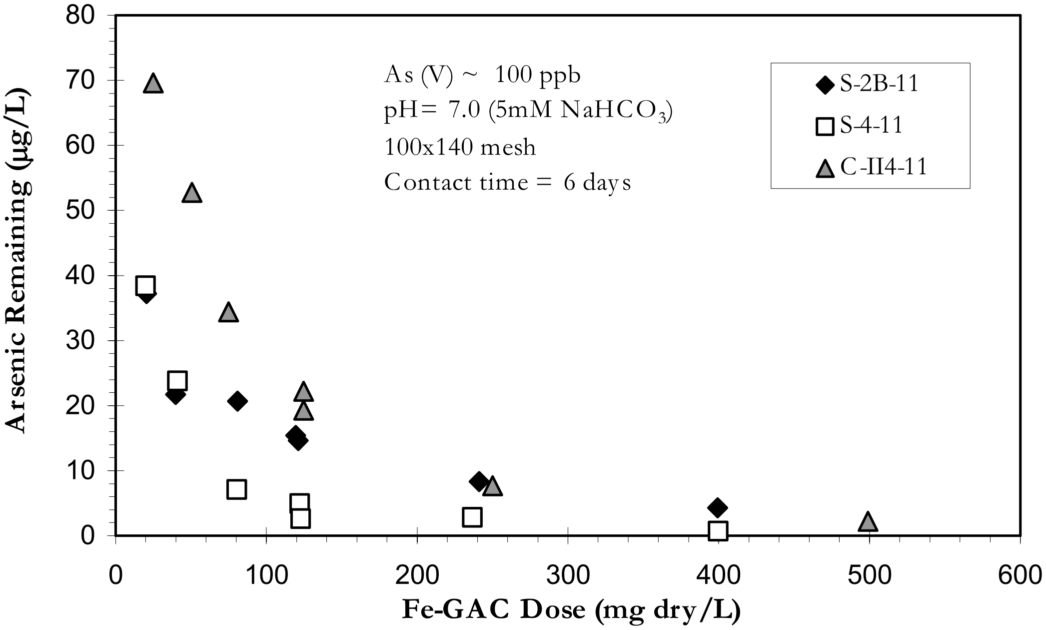


Figure 3.10 Adsorption test in model solution for arsenic removal using Fe-GAC media from Solmetex and Clemson University

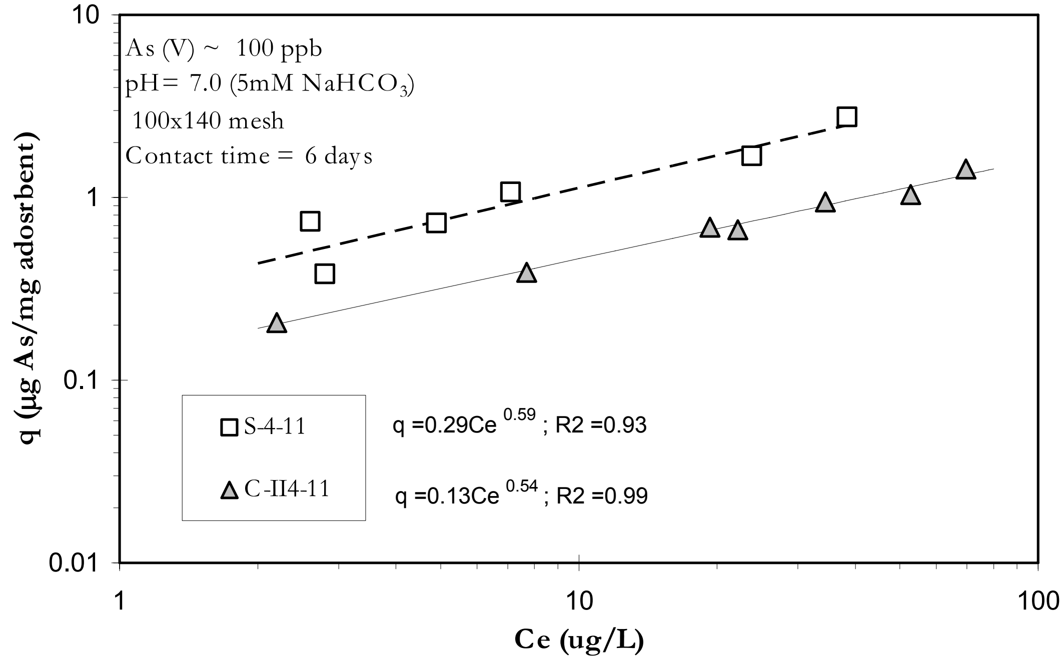


Figure 3.11 Isotherm test comparing best performance Fe-GAC composites for arsenate removal in nanopure water from Clemson University and Solmetex. July 2005

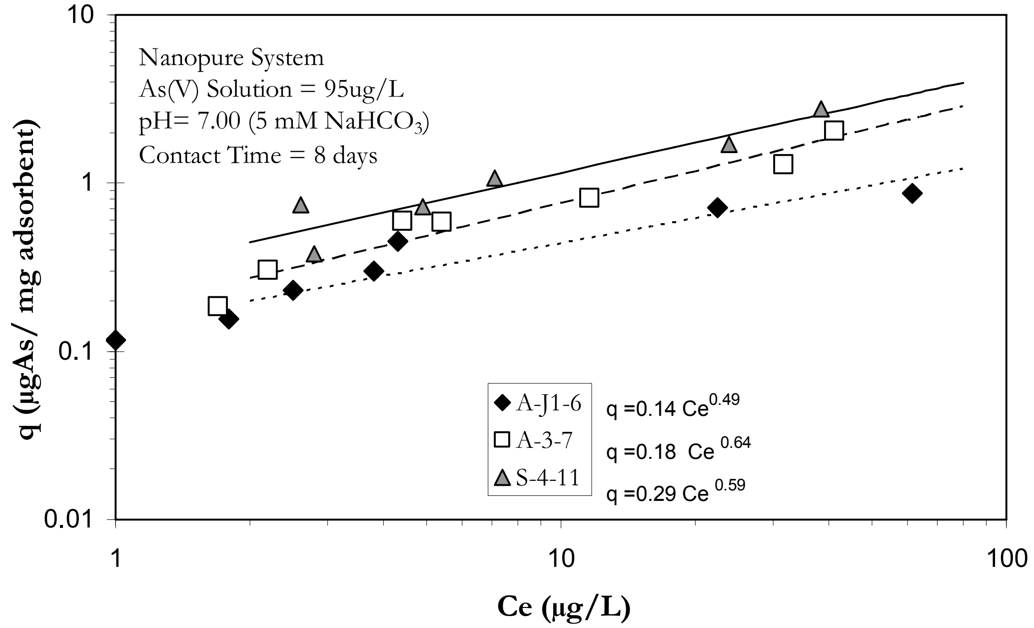


Figure 3.12 Log version of isotherm in a model solution using ASU produced composites and S-4-11 from Solmetex. Media was a 100x140 mesh size.

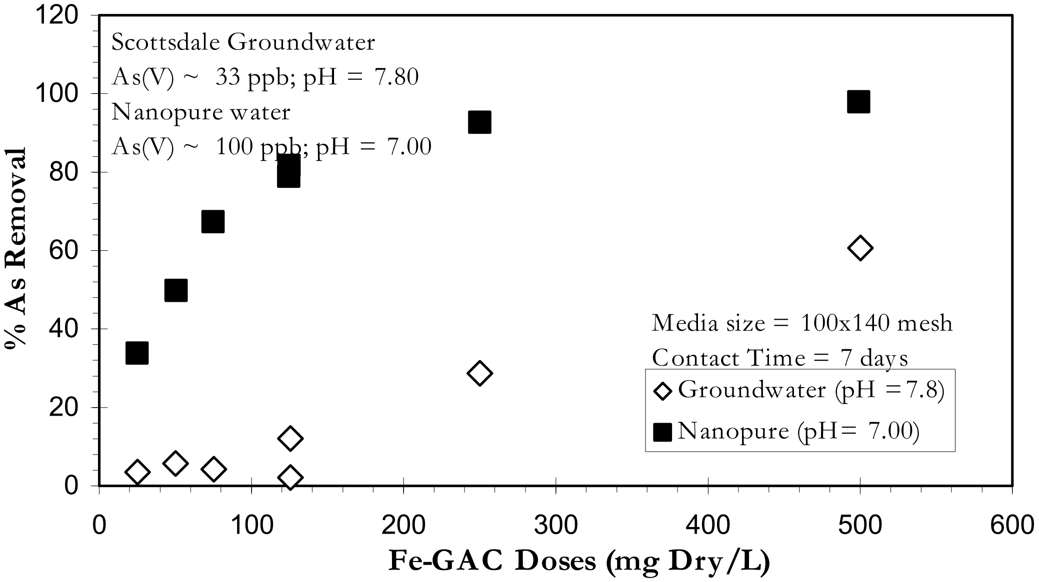


Figure 3.13 Adsorption test in Scottsdale groundwater with C-II4B-3 from Clemson University.

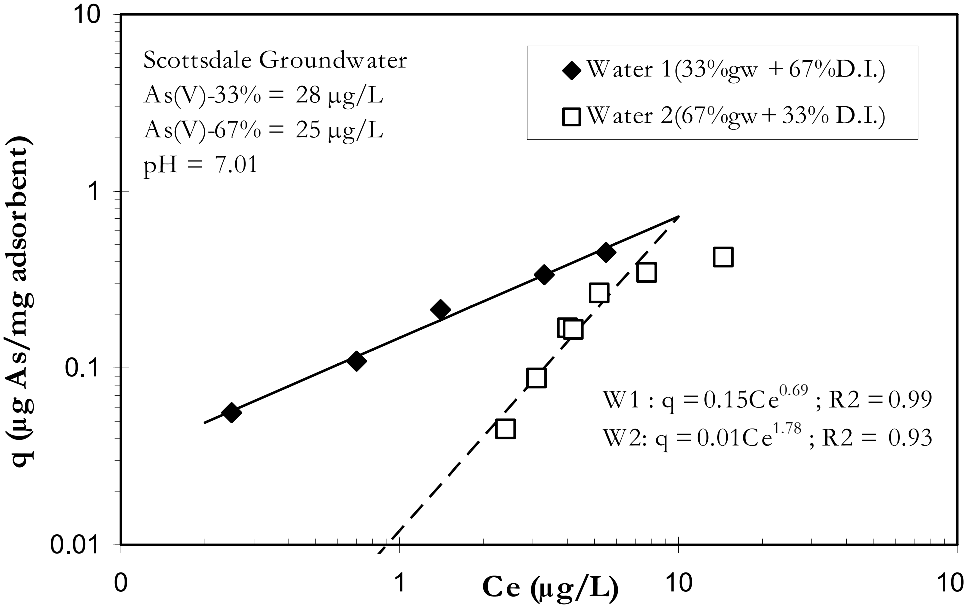


Figure 3.14 Effect of natural water matrix composition on competition and removal of As(V) using 33% or 67% Scottsdale Site 4E groundwater blended with DI water. As(V) spiked to nearly equivalent concentrations to that of the ambient groundwater (23-28 ppb). S-1-7 and S-2-4 were combined in these tests. 100x140 mesh material was used.

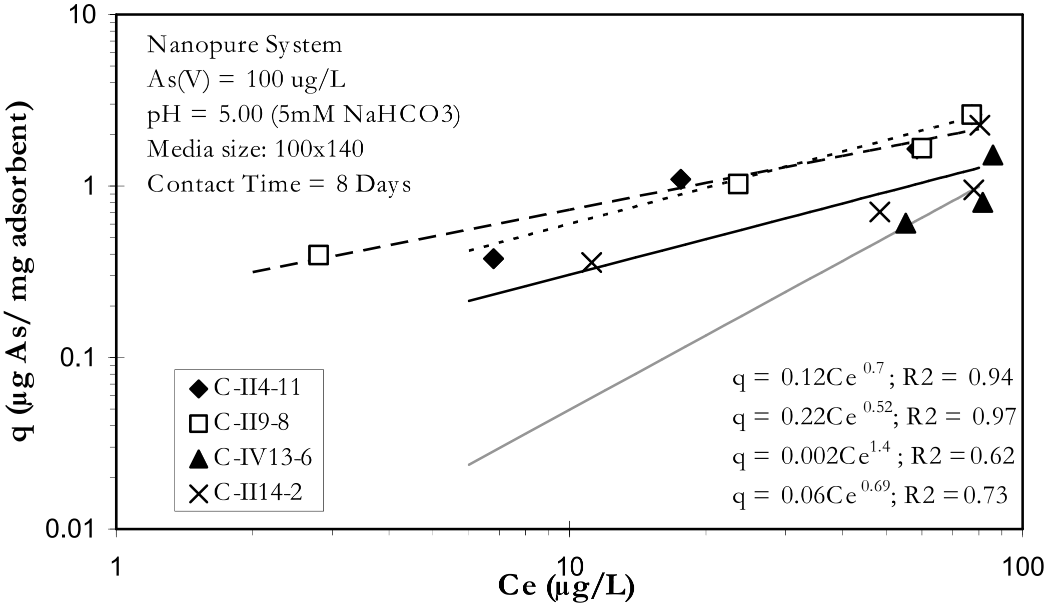
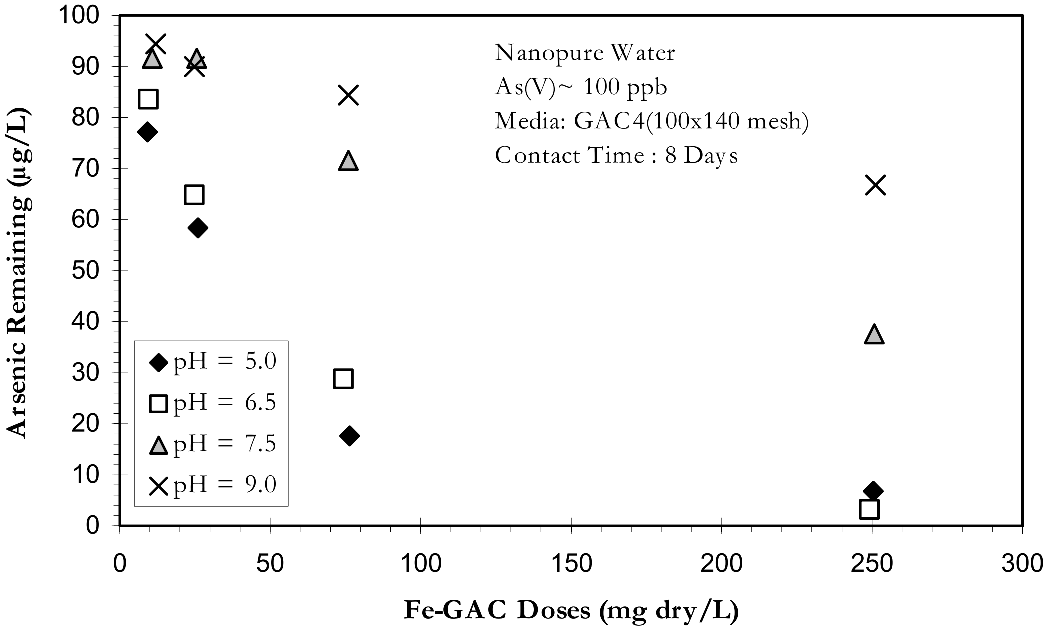


Figure 3.15 Effect of pH on arsenate adsorption by Fe-GAC media from Clemson University



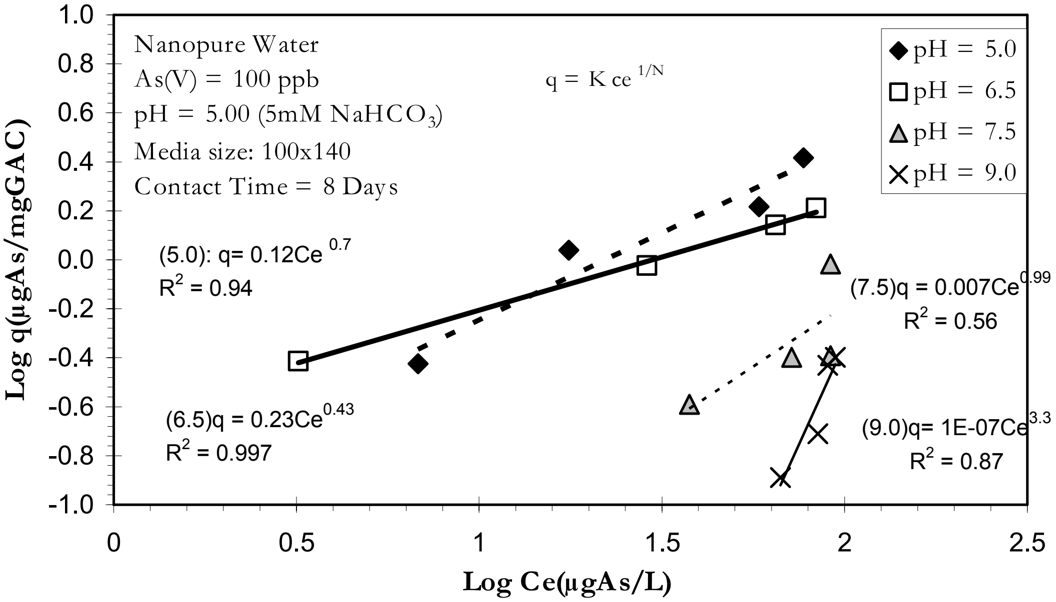


Figure 3.16 Comparison of arsenic removal as a function of pH with C-II4B-3 (similar trends observed for samples #9, 13, and 14) in nanopure water

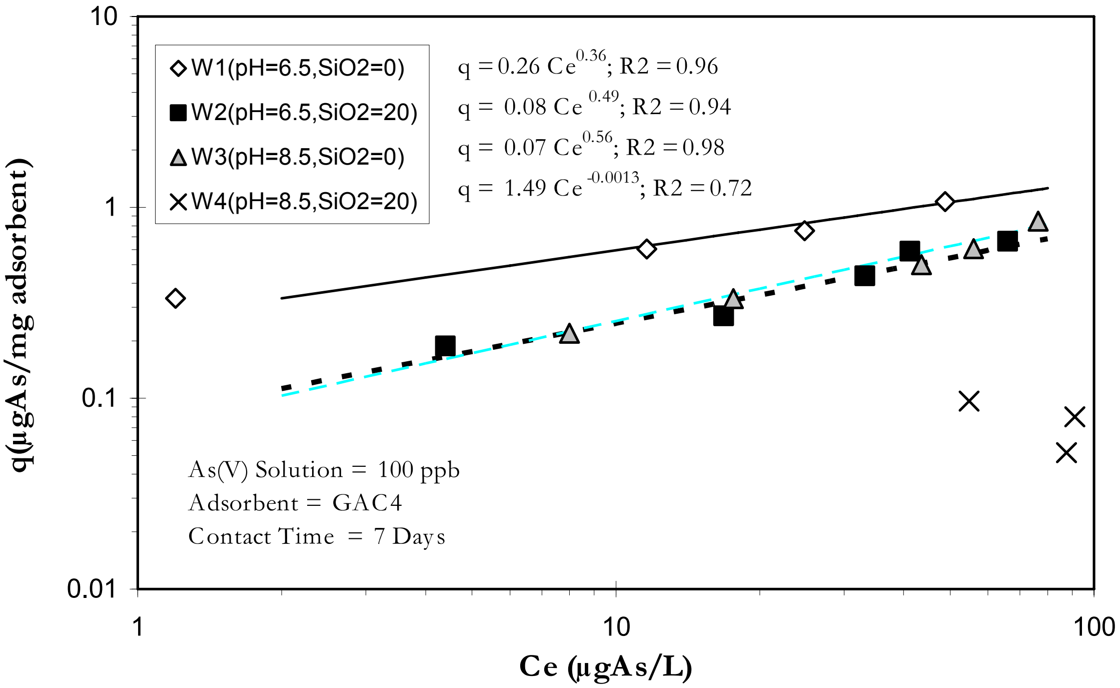


Figure 3.17 Effect of pH and silica on As(V) removal using a base NSFI challenge water matrix (contact time = 7 days)

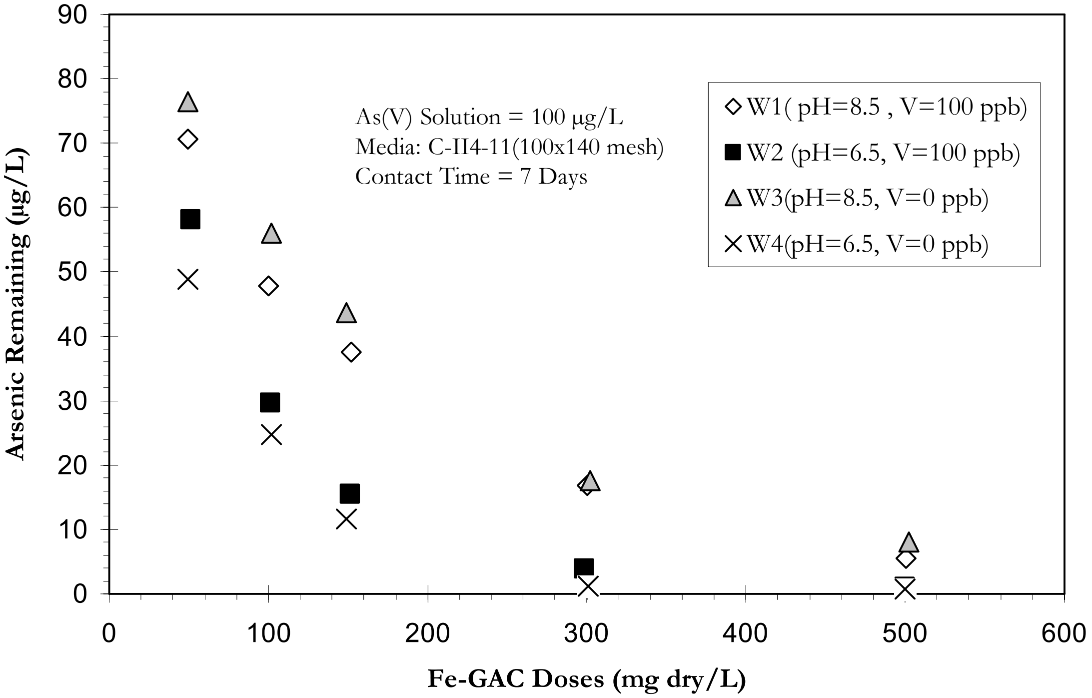


Figure 3.18 Effect of pH and vanadium on As(V) removal using a base NSFI challenge water matrix (contact time = 7 days)

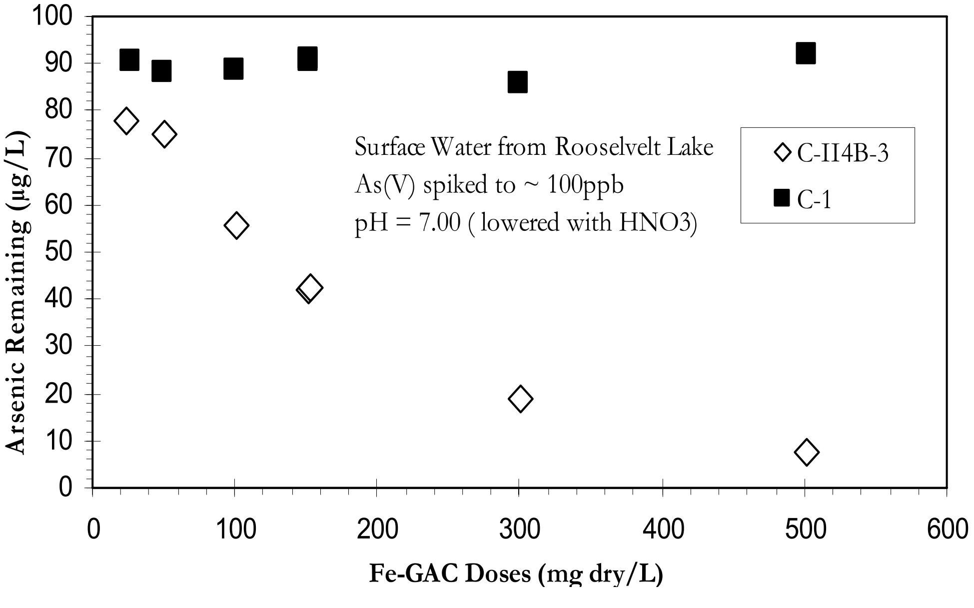


Figure 3.19 Isotherm test in Rooselvelt Lake water. Media mesh size was 100x140

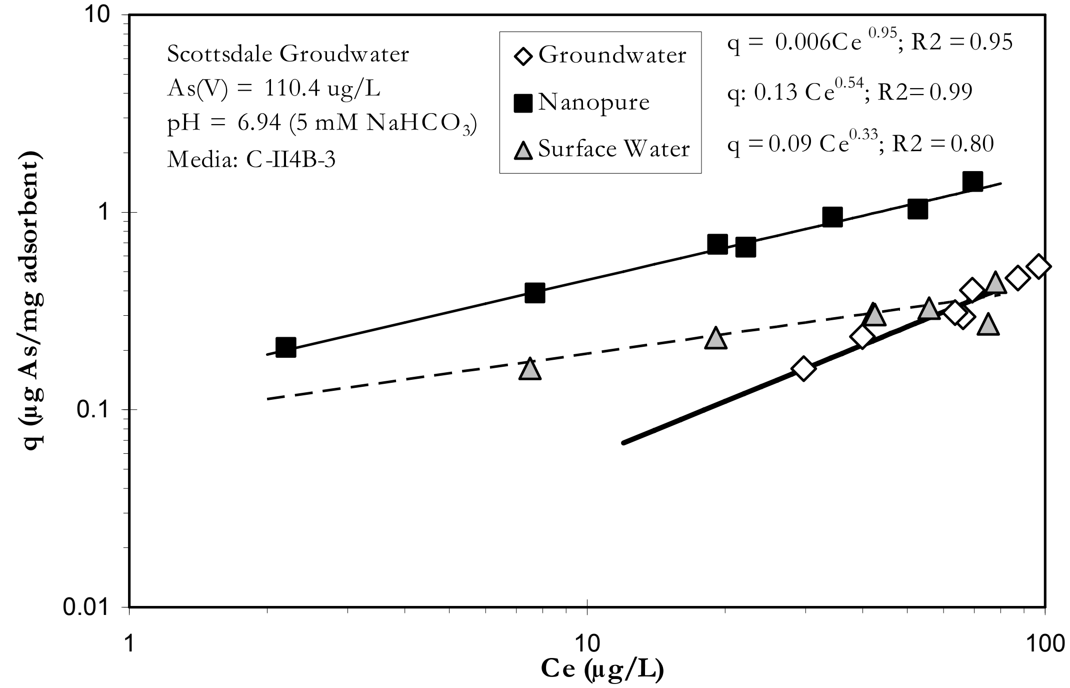


Figure 3.20 Comparison of media performance for arsenate removal in different water systems. All three cases are from different batch experiments at pH of 7

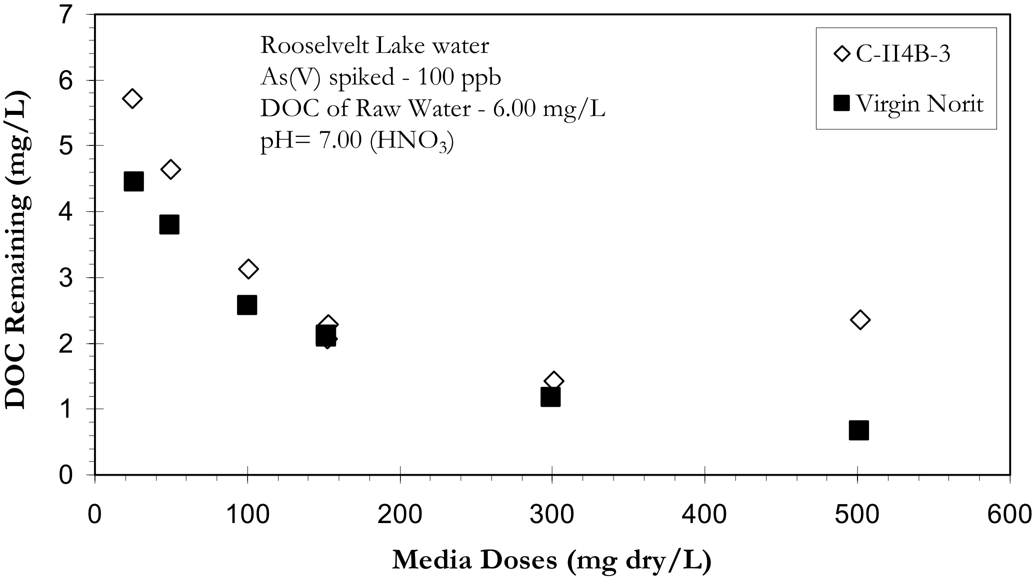


Figure 3.21 Comparison of C-II4B-3 and virgin GAC for DOC removal in surface water

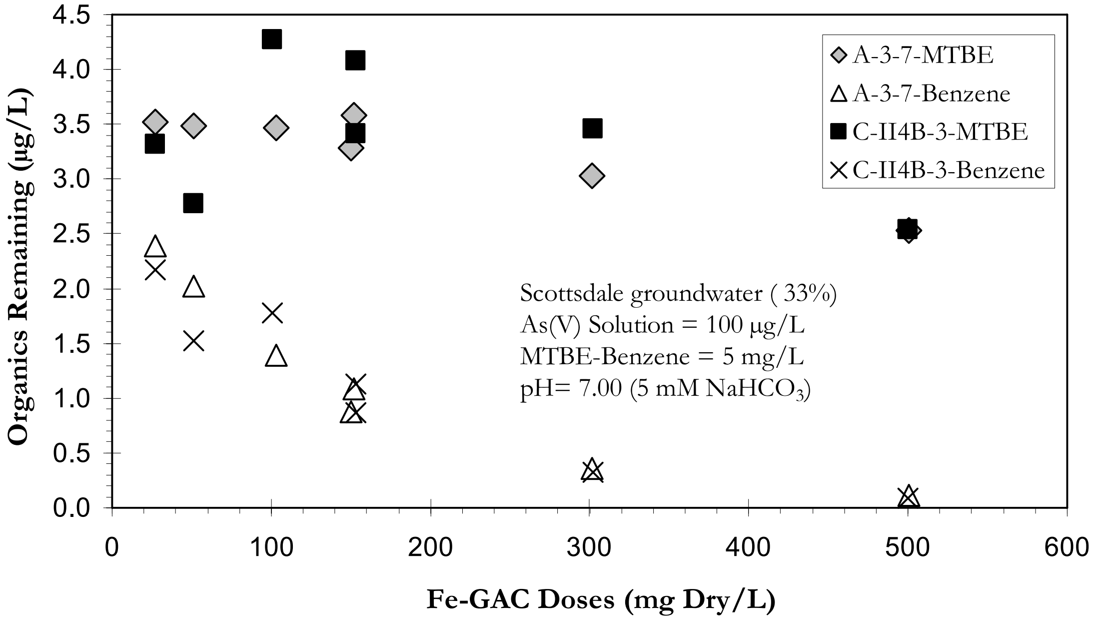


Figure 3.22 Adsorption of SOCs (MTBE and benzene) from groundwater (blended at 33% with nanopure water) containing arsenate by several Fe-GAC materials.

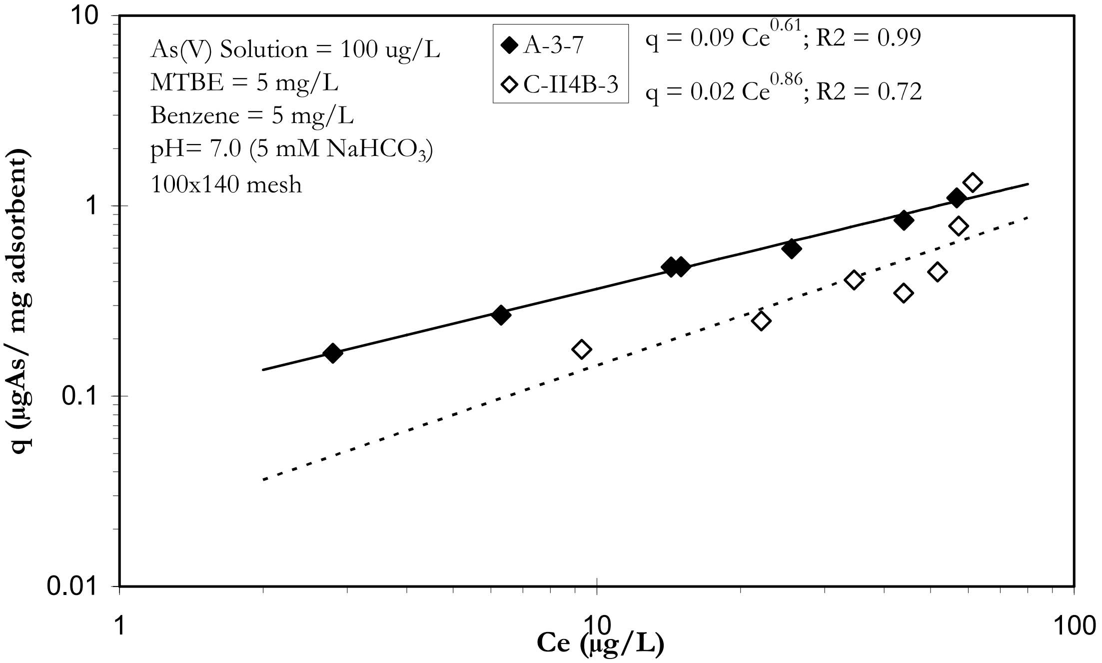


Figure 3.23 As(V) adsorption in groundwater (33% natural, 67% nanopure) spiked with SOCs by Fe-GAC materials from Clemson University and ASU (Solmetex process)

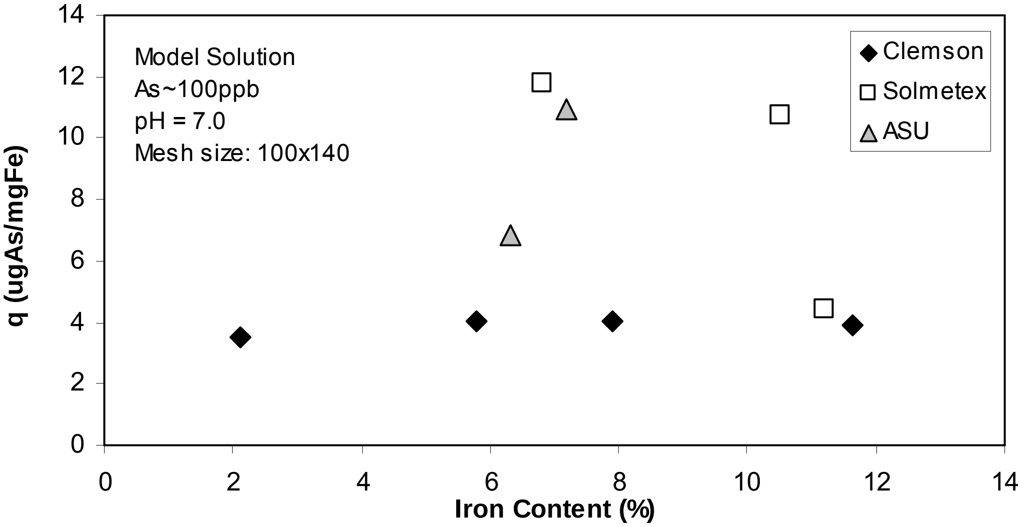


Figure 3.24 Summary of Fe-GAC performances removing arsenate in model solutions based on iron content. Adsorption densities for Clemson University, Solmetex and ASU composites were calculated at final arsenic concentrations of 10 ppb.

CHAPTER 4 ARSENIC REMOVAL IN CONTINUOUS FLOW COLUMN TESTS

Rapid Small Scale Column Tests (RSSCTs) were conducted using Arizona groundwater collected from the City of Scottsdale (4E site). This water typifies groundwaters in the southwestern USA impacted by the arsenic regulation and contains ~25 µg/L of arsenic, low DOC (<1 mg/L), pH of 8.5, alkalinity ~156 mg $CaCO_3$/L, total dissolved solids (TDS) of ~800 mg/L, vanadium of 80 µg/L and silica of 30 mg/L. RSSCTs were conducted in parallel, allowing comparison for different media on a common influent water source.

FE-GAC MEDIA PERFORMANCE WITH CLEMSON UNIVERSITY FE-GAC COMPOSITES

Based on prior batch adsorption experiments conducted (Chapter 3), several Fe-GAC composites from Clemson University were selected to compare performance in a more dynamic system (continuous flow column tests). RSSCTs were scaled (Table 4.1) to simulate a pilot scale column having an EBCT of 2.5 minutes and a loading rate comparable with that employed for GFH or E33 (~8 gpm/ft^2). A Reynold Schmidt product of 1000 was used. 12x40 mesh size full-scale media was used in the scaling analysis. RSSCT results for four Fe-GACs are presented in Figure 4.1. C-II4-11 and C-II9-8 exhibited a short lag period of near complete arsenic removal, before arsenic breakthrough. Arsenic breakthrough was reached after approximately 500 to 1000 BV.

C-II4-11 and C-II9-8 performed better than C-IV13B-6 or C-II14-2. This conclusion was consistent with the pattern observed from batch experiments (Chapter 3, Fig. 3.4 and 3.8). An isotherm was also conducted on this same water using C-II4-11 (Figure 6.13). The arsenic adsorption was significantly lower than would have been expected from the isotherm test for C-II4-11 in nanopure water (Figure 3.7-3.8), suggesting that competing ions were present in the water that affected the performance of the Fe-GAC in the RSSCT. An effluent arsenic concentration of 10µg/L was reached immediately for samples 13B and #14, and after ~500 bed volumes for samples 4 and 9.

For comparison, GFH or E33 would be expected to treat approximately 20,000 bed volumes before reaching 10 µg/L on a comparable groundwater. However, the results of Fe-GAC isotherm adsorption densities were also approximately an order of magnitude lower than GFH or E33, so the duration of arsenic removal in the RSSCTs is not unexpected.

EFFECT OF EBCT

Scottsdale 4E groundwater blended to 33% with nanopure water (77% of final volume) was used for these experiments, with an adjusted pH of 7.0 and spiked with sodium arsenate to reach ~25 ppb. These RSSCTs with 100x140 mesh size materials were conducted simulating a full scale system with the following operating characteristics (radius 0.513 mm, loading rate of 4.1 gpm/ft^2) with a Re-Sc value of 1000 and using proportional diffusivity scaling equations as stated before, (Table 4.1). EBCT$_{LC}$'s from 2.5 to 10 minutes were tested.

Clemson University Fe-GAC Composites

C-II4-11 (100x140 mesh size) was one of the best performing media, so Clemson University prepared a larger mass of a similar material (C-II4B-3). This material was used in subsequent tests. For EBCT of 4 and 10 minutes the columns were operated in parallel but were fed from different tank containers.

Figure 4.2 presents the results of both tests using an EBCT of 4 -min and 10 min. Prior RSSCT at EBCT of 2.5 was plotted as a reference. The 10 minute EBCT experiment had a slightly different breakthrough curve than the 4 minute EBCT. Both reached 10 ppb As(V) in the effluent after approximately 5000 bed volumes. Complete break through was reached after 15,000 bed volumes.

Solmetex Fe-GAC Composites

RSSCTs were conducted with S-1-7 for the 4 minute EBCT and a mixture of S-1-7 and S-2-4 as used in one batch isotherm test (Figure 6.14). From past batch adsorption experiments (Figure 3.6) it appeared that S-1-7 and S-2-4 would have very similar performance. There was insufficient mass of S-1-7 alone to conduct a RSSCT with a simulated EBCT of 10 minutes**.** The influent water contained 33% Scottsdale Site 4E groundwater plus 67% nanopure water, adjusted to pH 7.0 with $NaHCO_3$ and spiked with sodium arsenate to ~25 ppb.

Arsenic breakthrough curves as a function of bed volumes (BV) treated are shown in Figure 4.3. At a 4 minute simulated EBCT approximately 15,000 BV were treated before reaching 10 ppb, whereas 22,000 BV were treated at 10 minutes before reaching 10 ppb effluent arsenic. This represents a 46% increase in treated bed volumes with the longer EBCT. The area above the arsenic breakthrough curves for 4 and 10 minute EBCTs would be equal for a synthetic organic compound on GAC alone.

COMPARISON OF FE-GAC COMPOSITES

To facilitate direct comparison of different Fe-GAC media (Clemson University, Solmetex LLNL and ASU) performance, four RSSCTs with an EBCT$_{sc}$ designed to simulate a full-scale system with EBCT$_{LC}$ of 4 minutes (Table 4.1) were conducted in parallel from a common water source. Scottsdale groundwater was blended with 33% GW plus 67% nanopure water and As(V) spiked to 25 µg/L with sodium arsenate. pH of this water was lowered to 7.00 with CO_2.

Figure 4.4 presents the results. The aerogel Fe-GAC composite from LLNL (L-294-1) and the sample from Clemson University (C-II4B-3) had similar breakthrough curves and exhibited complete breakthrough after ~15,000 bed volumes. Two Fe-GAC composites produced by ASU using the Solmetex process on Jacobi base material (A-J1-6) and Norit HD3000 (A-3-7) achieved significantly longer operational run times. A-J1-6 operated for approximately 65,000 bed volumes before approaching the influent As(V) concentration. Even after 70,000 bed volumes A-3-7 only had reached 60% of the influent As(V) concentration. Some of the variations from a smooth breakthrough curve occurred as two of the columns (A-J1-6 and A-3-7 at 22,000 bed volumes) were temporarily turned off for a day while new water was collected. Overall, the Fe-GAC composites produced using the Solmetex process, which yield ~8% to 10% iron content by dry weight, appear to have the greatest capacity for arsenic removal.

CONCURRENT ARSENIC AND ORGANIC REMOVAL

RSSCTs with As(V) and MTBE (polar compound) and benzene (non-polar compounds) in solution were conducted to test the potential of Fe-GAC composites (A-3-7 and C-II4B-3) for removing both SOCs and arsenic in a more dynamic system. Once again Scottsdale groundwater blended at 33 % with DI water was used for these experiments adjusting pH of the water to 7.00 with HNO_3. As(V) at 25 ppb, MTBE at 2.8 ppm and benzene at 1.5 ppm concentrations were all spiked into the feed-water. 10 mM $NaHCO_3$ was added and the pH adjusted to 7.0. Over the course of the RSSCT run, SOC concentrations in the influent tank were observed to decrease slowly by ~40% based upon daily measurements.

Figure 4.5 presents breakthrough curves for As(V). A-3-7 achieved better arsenic removal than sample C-II4B-3, treating ~25,000 bed volumes (4000 bed volumes for C-II4B) before exhibiting a tailing breakthrough curve. Both Fe-GAC composites had similar GAC base materials (Norit HD3000) and achieved comparable MTBE and benzene removal (Figure 4.6). C-II4B-3 treated almost 5000 bed volumes before complete breakthrough for MTBE while A-3-7 treated around 2000 bed volumes. For benzene, C-II4B-3 reached complete breakthrough after 15,000 bed volumes whereas A-3-7 broke through at 8000 bed volumes. As expected the more polar compound (MTBE) broke through much sooner than the more hydrophobic compound (benzene) Figure 4.6.

SUMMARY

An initial RSSCT was conducted with Fe-GAC composites from Clemson University using Scottsdale groundwater at pH 7.8, arsenate concentration of 33 ppb and $EBCT_{LC}$ of 2.5 minutes. The following observations were made:

- Arsenic breakthrough for C-II4-11 and C-II9-8 was reached after approximately 500 to 1000 bed volumes
- The pattern of media performance was consistent with prior screening tests and batch isotherm experiments in both a model solution and natural waters.

Additional RSSCTs using Scottsdale groundwater blended with nanopure water, pH of 7.0 and arsenate concentration of ~25 ppb were conducted. The following observations were made:

- When using C-II4B-3 as adsorbent, the 10-minute $EBCT_{LC}$ experiment had a slightly longer runtime breakthrough curve than the 4-minute $EBCT_{LC}$. Both reached 10 ppb As(V) in the effluent after approximately 5000 bed volumes. Complete break-through was reached after 15,000 bed volumes
- Two Fe-GAC composites (S-1-7 and S-1&2) were used to assess the impact of $EBCT_{LC}$ (4- and 10-minute) on As(V) removal. $EBCT_{LC}$ of 4-minutes approximately 15,000 BVs were treated before reaching 10 ppb, whereas 22,000 BV were treated with an $EBCT_{LC}$ of 10-minutes. This represents a 46% longer runtime with the longer $EBCT_{LC}$.

Four Fe-GAC composites were evaluated in RSSCTs with $EBCT_{LC}$ = 4-minutes and a common influent water source. The influent water source was Scottsdale groundwater was blended to achieve 33% GW and 67% nanopure water before spiking in 25 μg/L As(V). pH of this water was lowered to 7.00 with CO_2. The following was observed:

- L-294-1 and C-II4B-3 had similar breakthrough curves and exhibited complete breakthrough after ~15,000 bed volumes
- A-J1-6 operated for approximately 65,000 bed volumes before approaching the influent As(V) concentration. Even after 70,000 bed volumes A-3-7 only had reached 60% of the influent As(V) concentration.

RSSCTs with Scottsdale groundwater blended at 33% with 67% nanopure water were conducted for concurrent arsenic and SOCs removal. pH of the water was 7.0 and As(V), MTBE and benzene were all spiked into the feed-water. The following was observed:

- A-3-7 achieved higher arsenic removal than sample C-II4B-3, treating ~25,000 bed volumes compared to 4000 bed volumes with C-II4B-3, before exhibiting a tailing breakthrough curve
- C-II4B-3 treated almost 5000 bed volumes before complete breakthrough for MTBE while A-3-7 treated around 2000 bed volumes before complete breakthrough
- For benzene C-II4B-3 reached complete breakthrough after 15,000 bed volumes whereas A-3-7 reached complete breakthrough at 8000 bed volumes.

Table 4.1 RSSCT design parameters for EBCT of 2.5, 4 and 10 minutes

Design Parameters	Simulated Pilot Scale	RSSCT (PD)	Simulated Pilot Scale	RSSCT (PD)	Simulated Pilot Scale	RSSCT (PD)
Input Parameters	EBCT$_{LC}$ = 2.5 min		EBCT$_{LC}$ = 4 min		EBCT$_{LC}$ = 10 min	
Particle radius (cm)	0.0513	0.0064	0.0513	0.0064	0.0513	0.0064
Column diameter (cm)	30.48	1.10	30.48	1.10	30.48	1.10
Column area (cm^2)	729.29	0.9499	729.29	0.9499	729.29	0.9499
Wet density (g/mL)	1.79	1.40	1.79	1.40	1.79	1.40
EBCT (min)	2.50	0.31	4.00	0.50	10.00	1.25
Loading rate (m/h)	20.21	7.03	10.11	7.03	10.11	7.03
Loading rate (cm/min)	33.69	11.72	16.85	11.72	16.85	11.72
BV to be processed	30000	30000	30000	30000	30000	32000
Flow rate (gpm)	6.50		3.25		3.25	
Flow rate (gpm/ft^2)	8.28		4.14		4.14	
Re*Sc (200,000-200)		1000		1000		1000
U (Pa s)	8.94E-04	0.00	8.94E-04	0.00	8.94E-04	0.00
P (kg/m^3)	1000	1000	1000	1000	1000	1000
D_L (Liquid diffusivity) (m^2/s)	1E-09	0.00	1E-09	0.00	1E-09	0.00
d (m)	0.00103	0.00	0.0010	0.00	0.0010	0.00
v (m/s)	0.00562	0.00	0.0028	0.00	0.0028	0.00
e (porosity)	0.25	0.25	0.25	0.25	0.25	0.25
Re	25.8	1.12	1.30	1.12	1.3	1.12
Sc	893.7	893.7	893.7	893.7	893.7	893.7
Re*Sc	23044.2	1000	11522	1000	11522.1	1000
Design Data						
Flow rate (mL/min)	24570	11.13	12285	11.13	12285	11.13
Volume of media (mL)	61425	3.5	49140	5.6	122850	13.9
Length of the column (cm)	85.34	3.7	85.34	5.8	85.34	14.6
Mass of the media (gm)	109950.7	4.9	87960.6	7.8	219901.5	19.4
Water required (L)	1842750	104.2	1474200	166.6	3685500	444.4
Water required (gals)	487500	27.6	390000	44.1	975000	117.6
Duration of test (days)	52.08	6.5	83.3333	10.4	208.333	27.7

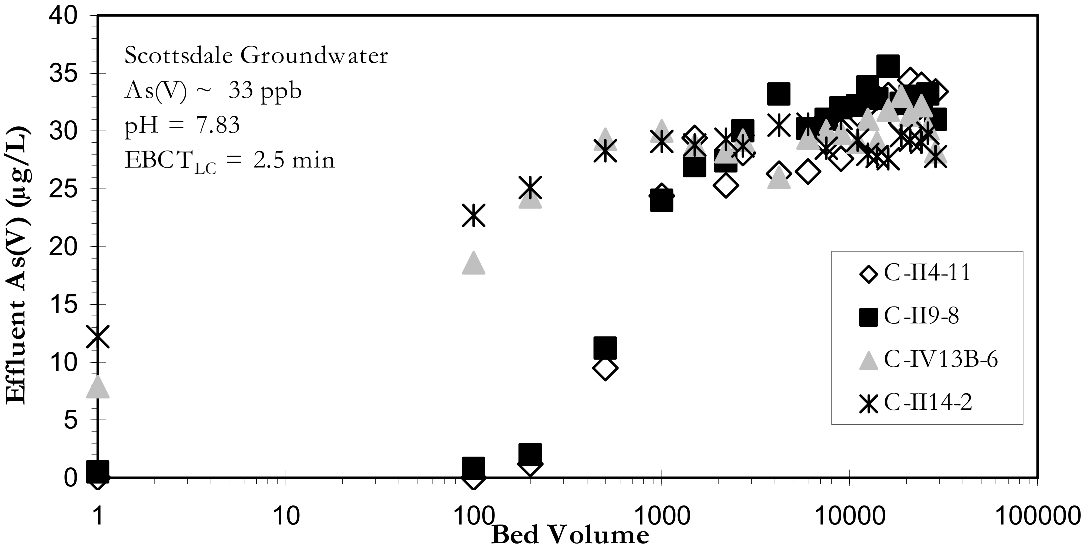


Figure 4.1 RSSCTs with Fe-GACs from Clemson University in Scottsdale groundwater

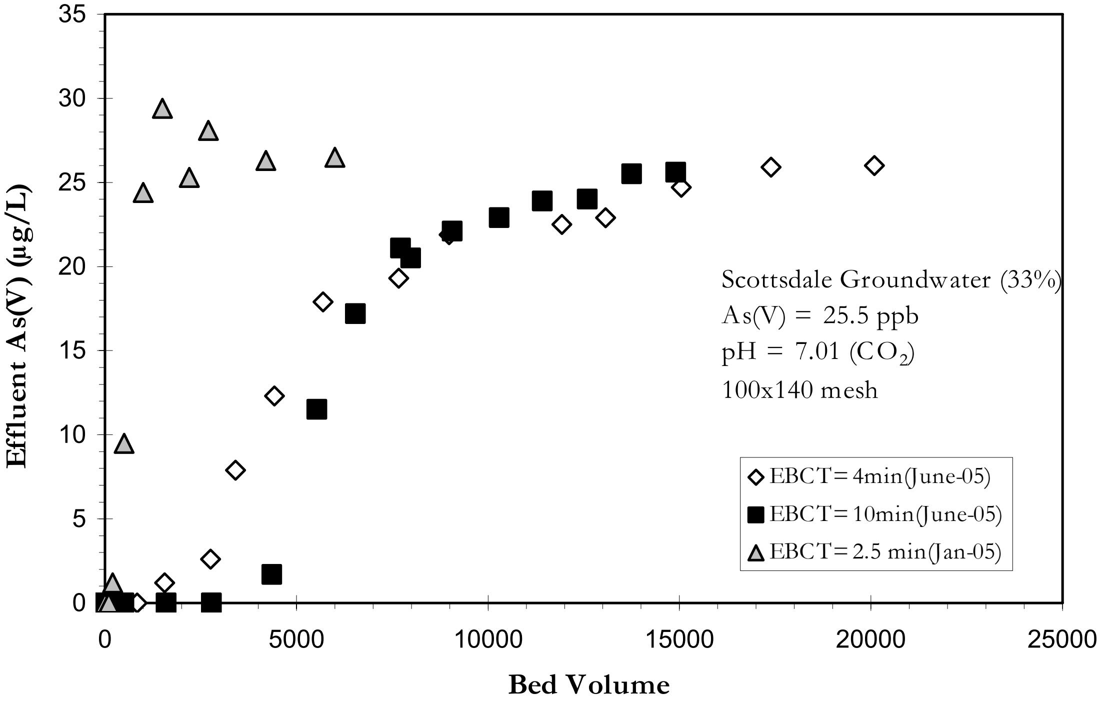


Figure 4.2 Effect of EBCT$_{LC}$ on As(V) breakthrough with C-II4B-3 (100% groundwater, pH= 7.8 and 33 µg/L of arsenate).

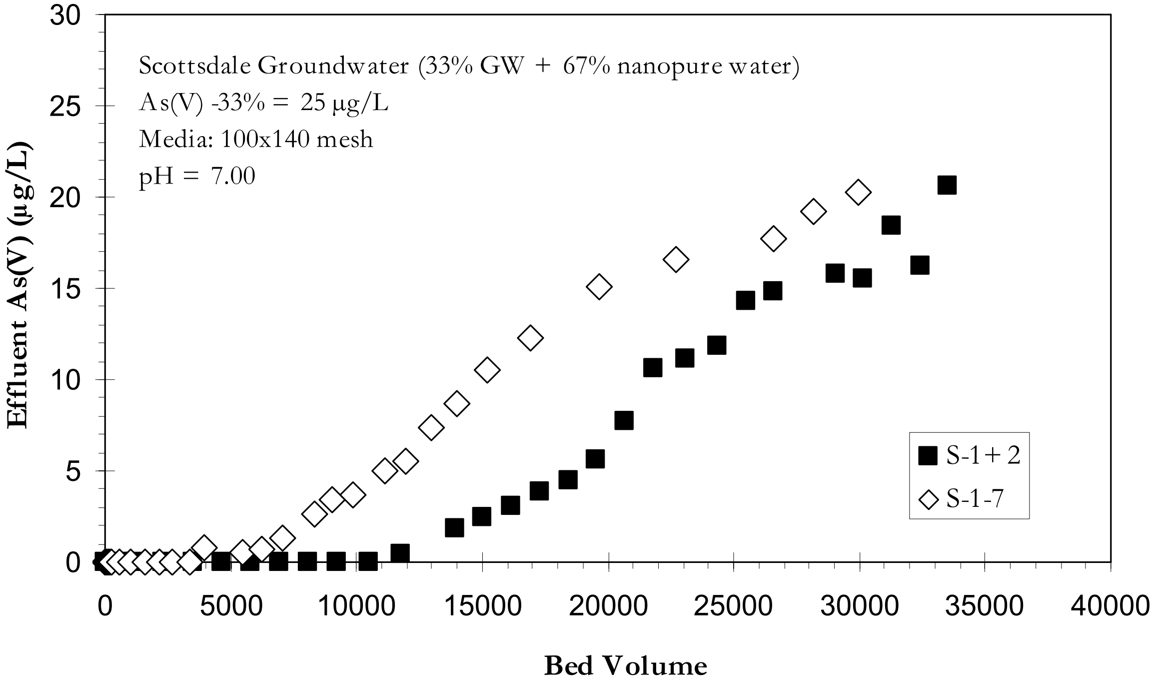


Figure 4.3 Arsenic breakthrough curves for RSSCTs using S-1-7 (EBCT$_{LC}$= 4 min) and a blend (S-1&2) of S-1-7 and S-2-4 (EBCT$_{LC}$ = 10 minute) (100x140 mesh)

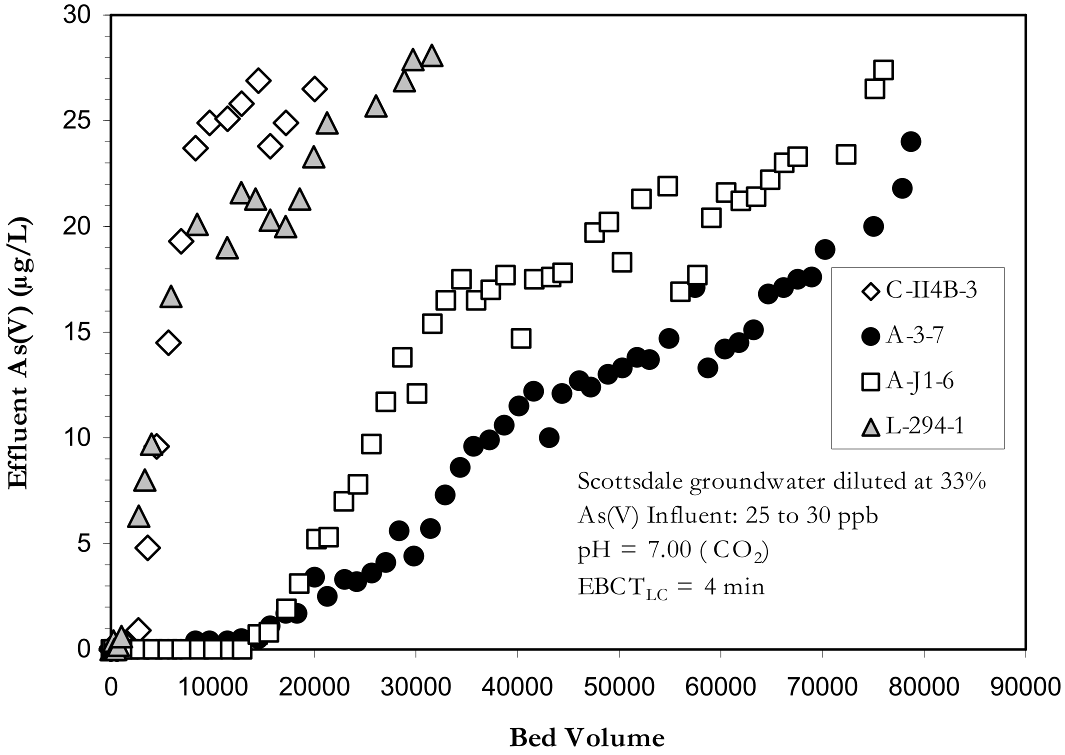


Figure 4.4 Arsenic breakthroughs by four Fe-GAC composites. RSSCTs run in parallel from common water source. 33% of Scottsdale groundwater plus 67% nanopure water was used. All media were 100x140 mesh size.

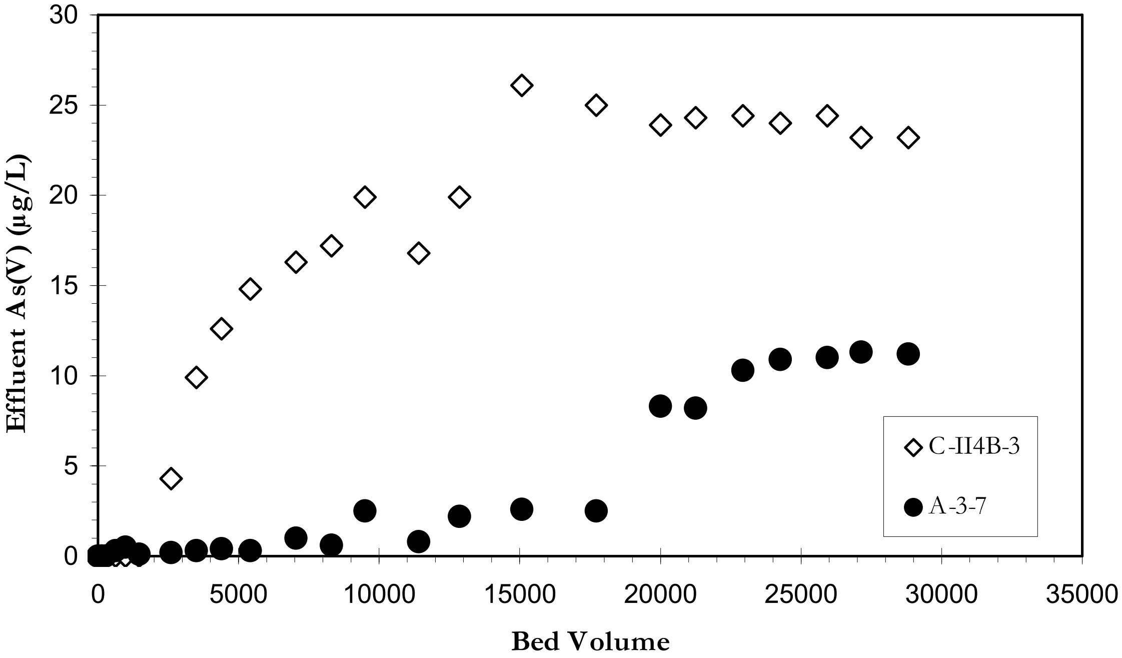


Figure 4.5 RSSCTs for As(V) removal in modified Scottsdale groundwater (33% groundwater + 67% nanopure water) spiked with SOC using Fe-GACs from Clemson University and ASU (EBCT$_{LC}$=4 min)

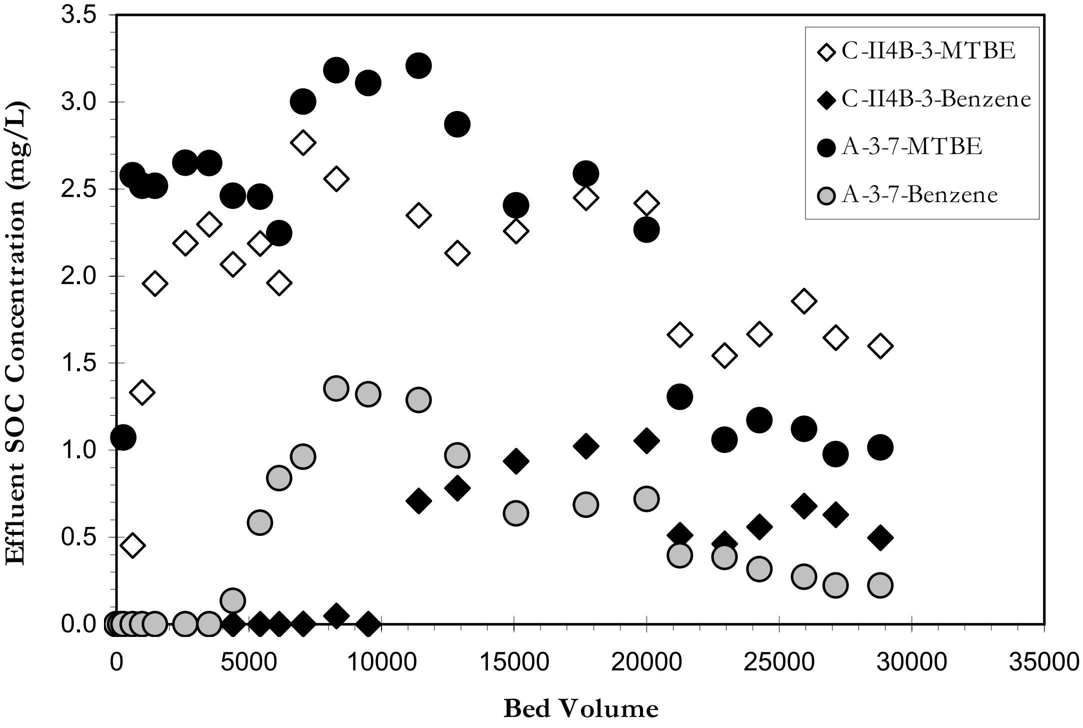


Figure 4.6 Concurrent As(V) and SOC removal by two Fe-GAC composites. Initial MTBE and benzene concentrations were 2.8 mg/L and 1.5 mg/L, respectively.

CHAPTER 5 DISCUSSION OF RESULTS

This chapter presents a discussion of results obtained for arsenic adsorption by Fe-GAC composites in both batch isotherm experiments and RSSCTs. The chapter is subdivided into experiments with either model solutions or groundwaters. Finally, the observed test results are related with available characterization data for the media.

BATCH AND RSSCT ADSORPTION CAPACITIES

Adsorption data were interpreted using the Freundlich model (Faust and Hoigne 1987). The linearization of the log vs. log data indicated reasonable application of the model to this work. Evaluation of performance of the composites tested was represented by the following equation.

$$q_o = K\, C_e^{\,1/N} \tag{5.1}$$

where q_o is arsenic adsorption density on the media (μg/mg), C_e is the equilibrium arsenic concentration in solution (μg/L), 1/N is the adsorptive intensity constant, and K is the adsorptive capacity constant $(\mu g/mg)/(\mu g/L)^{1/N}$. Batch adsorption tests were conducted to evaluate Fe-GAC composites for As(V) removal in model solutions and groundwaters. The iron content and values for isotherm parameters for the different Fe-GACs tested in model solutions are summarized in Table 5.1.

Adsorption capacities were also calculated from RSSCTs. Adsorption densities (q_o in μgAs/mg dry-mass of GAC) from column studies were calculated based upon the area above the As(V) breakthrough curve, volume of the packed bed, and mass of Fe-GAC in the packed bed (Table 5.2). Based upon the iron content q_o values were calculated at C_e of 10 μg/L and at C_e=C_o where C_o is As(V) concentration at the influent.

Model Solutions

Preliminary kinetic studies and batch screening tests in model solutions demonstrated the order of efficiency of different Fe-GAC composites from Clemson University and Solmetex for arsenic removal. C-II4-11>C-II9-8>C-IV13-6>C-II14-2 removed more arsenic than other Clemson University media. C-II4-11 and C-II9-8 (both ferrihydrate) have higher iron content (11% and 8%) than C-IV13-6 and C-II14-2 (6% and 2%) however the latter have larger surface area and higher pore distribution than C-II4-11 and C-II9-8 (Table 3.2).

Subsequent isotherm tests with S-1-7 and S-4-11 in parallel with C-4II-11 (Norit HD3000 GAC based) demonstrated better arsenic adsorption capacity for the Solmetex composites. K values for S-1-7 and S-4-11 are 0.22 and 0.29 $(\mu g/mg)/(\mu g/L)^{1/N}$, respectively. C-II4-11 had a K value of 0.13 (Table 5.1).

Isotherm tests with Fe-GACs prepared by ASU and the best Fe-GAC media from Solmetex Inc. were conducted for comparison. S-4-11 had a higher adsorption capacity (K = 0.29(μg/mg)/(μg/L)$^{1/N}$) than A-3-7 and A-J1-6 (K values of 0.18 and 0.14(μg/mg)/(μg/L)$^{1/N}$ respectively). S-4-11 and A-3-7 were Norit HD3000 GAC based. A-J1-6 was Jacobia GAC based. These Fe-GAC samples from ASU and Solmetex were prepared with the same treatment approach for iron deposition. It can be argued that the difference in arsenic adsorption capacities might rely on both the iron content and treatment for each composite. S-4-11 contains 10.5% Fe, A-3-7 contains 7.2% Fe and A-J1-6 contains 6.3% Fe.

Overall results from isotherms in model solutions showed that S-4-11, A-3-7, A-J1-6 and C-II4-11 had the best arsenic adsorption capacities with 1.13, 0.79, 0.43 and 0.45 μgAs/mg-adsorbent, respectively. Based on these results C-II4-11 was selected to perform extensive RSSCTs and for this goal a larger volume of this composite was prepared and provided by Clemson University. The new Fe-GAC was identified as C-II4B-3. Solmetex sample S-4-11 was not used for RSSCTs (among best media performance) due to lack of sufficient material for these experiments.

Groundwaters

Effect of natural water matrix composition on competition and removal of As(V) was evaluated in isotherm tests. Waters with 33% and 67% Scottsdale Site 4E groundwater blended with DI water were used. A combined mixture of S-1-7 and S-2-4 was used due to the limited availability of these media. Adsorptive capacities for As(V) were 0.15 and 0.01 (μg/mg)/(μg/L)$^{1/N}$ for 33% and 67% groundwaters respectively. These K values suppose greater competition of other ion constituents in the less blended groundwater and less blockage of pores on the GAC material by these ions in the more blended groundwater.

Initially, RSSCTs were conducted using samples from Clemson University in 100% groundwater from Scottsdale at $EBCT_{LC}$ of 2.5 minutes. C-II4-11 and C-II9-8 treated 500 bed volumes before reaching 10 ppb effluent arsenic. C-IV13-6 and C-II14-2 broke through almost immediately. The q_o value for C-II4 and C-II9 was 0.009 μgAs/mg dry-adsorbent at 10 ppb of As(V) in the column effluent confirming better adsorptive capacity than C-IV13 and C-II14 (q_o ~0 in both cases; Table 5.2). In batch experiments with model solutions the adsorption capacities for these composites were 0.45, 0.32, 0.23 and 0.07 μgAs/mg dry-adsorbent at As(V) Ce of 10 ppb, respectively. These results confirmed the trend observed for these media in screening and isotherm tests.

Table 5.3 summarizes the number of bed volumes processed in RSSCTs before reaching effluent As(V) concentrations of 10 or 20 μg/L. The number of bed volumes processed ranges from < 5 to nearly 75,000. Water quality and technique of iron impregnation affects this performance of the Fe-GAC materials.

The effect of water chemistry on As(V) removal by Fe-GACs was indirectly evaluated by RSSCTs. One set of RSSCTs were conducted with 100% Scottsdale groundwater at pH=7.8 using four Fe-GAC samples from Clemson University. One of the Clemson University media formulation (C-II4-11 & C-II4B-3)) was also evaluated in an RSSCT using blended Scottsdale groundwater (33% groundwater plus 67% nanopure water; pH of 7.0 and $EBCT_{LC}$ of 4 min). The higher value of q_o on the second study (~0.07 vs. 0.009 µgAs/mg-adsorbent) suggests that reducing the ion competition (silica, vanadium, phosphate, manganese, etc.) in the influent water plus reducing the pH and increasing the bed depth of the adsorbent (4min-$EBCT_{LC}$) increased the potential of the solute to be adsorbed to the Fe-GAC material. Other competing ions such as bicarbonate and hydroxide ions may also compete with arsenate for surface adsorption sites reducing surface diffusion mass transport.

Effect of EBCT on As(V) removal by Fe-GACs was also evaluated. C-II4B-3 from Clemson University and S-1-7 and S-(1+2) from Solmetex were used for column studies at different $EBCT_{LC}$ (4 and 10 minutes) in 33% of Scottsdale groundwater. Significant design parameters of these experiments are indicated in Chapter 4, Table 4.4.

C-II4B-3 had q_o values of 0.065 and 0.089 µgAs/mg dry GAC for $EBCT_{LC}$ of 4 and 10 minutes. S-1-7 had q_o values of 0.23 and 0.32 µgAs/mg dry GAC for $EBCT_{LC}$'s of 4 and 10 minutes. For both samples the adsorptive capacity for As(V) increases approximately 50% with increasing bed depth (Table 5.2). Since there is a benefit in the longer EBCT, a surface reaction may be rate limiting. Compared with iron (hydr)oxide commercial products (E33 or GFH) that have 100 to 250 m^2/g of surface area and 50% iron by dry weight, the Fe-GAC materials with >700 m^2/g appear to require longer EBCTs approaching times conventionally used for groundwater treatment (10 to 20 minutes).

Isotherm tests and RSSCTs were conducted to analyze co-adsorption of organics and arsenic. Initially C-II4B-3 and virgin Norit HD3000 GAC were tested in isotherm tests in surface water (Roosevelt Lake). As expected, C-II4B has higher As(V) adsorption capacity than the virgin GAC (Faust, S. D. and O. M. Aly 1987), but its efficiency was reduced by the presence of other constituents present in the water (natural organic matter). However, this test demonstrated that C-II4B and the virgin GAC have comparable adsorption capacities for DOC. These results indicate that Fe-GACs retain As(V) adsorption capacities when removing organics from water as well. Comparing C-II4B-3 capacity for As(V) removal in different water systems, results show that this media had better performance in Lake Roosevelt than in Scottsdale groundwater with q_o values of 0.19 and 0.06 µgAs/mg-adsorbent, respectively. These results suggest that ionic composition affects As(V) adsorption onto Fe-GAC; the groundwater has higher TDS than Lake Roosevelt.

Secondly, SOCs (MTBE and benzene) and arsenic removal was evaluated in isotherm tests conducted in parallel to RSSCTs. Isotherms show that A-3-7 and C-II4B-3 can remove As(V), MTBE and benzene from groundwater at the same time. Benzene though had more affinity than MTBE to be adsorbed to the Fe-GACs as observed in other investigations. Yet SOCs might reduce Fe-GACs adsorption capacities for As(V). Results showed that A-3-7 and C-II4B-3 had K values of 0.09 and 0.02(μg/mg)/(μg/L)$^{1/N}$, respectively for As(V). In model solutions these composites had K values of 0.18 and 0.13(μg/mg)/(μg/L)$^{1/N}$ without spiked SOCs. RSSCTs results confirmed those of isotherm tests. A-3-7 and C-II4B-3 demonstrated capacity for As(V) removal from water containing SOCs keeping the same order of efficiency as in isotherm tests. However presence of MTBE-benzene chemicals reduced arsenic adsorption of both samples approximately 31% and 43% (at 10 ppb of arsenate in the effluent) than when testing in the absence of these organics. This can be observed in the volume of water treated (Figures 4.4 and 4.5). In batch tests q_o values for A-3-7 and C-II4B-3 were 0.37 and 0.14 while in RSSCT these values were 0.35 and 0.05 μg/g at As(V) C_e of 10 ppb. These differences in adsorption capacities might indicate that SOCs and other chemicals contained in Scottsdale groundwater occupy considerable sites in the Fe-GAC material decreasing the rate of adsorption for As(V).

One last set of RSSCTs were conducted in parallel with several Fe-GACs for direct comparison of performances (Figure 4.4). Scottsdale groundwater at 33% was the water source and based on the effect of EBCT on mass transfer zone, an $EBCT_{LC}$ of 4 minutes was selected. A-3-7 and A-J1-6 had better As(V) removal with q_o values of 0.625 and 0.459 than C-II4B-3 and L-294-1 with 0.08 and 0.12 μgAs/mg dry-adsorbent at As(V) C_e of 10 ppb. Batch tests in model solutions indicated qo values of 0.79, 0.43, 0.25 and 0.06, for these composites, respectively. Iron content for these samples is 7%, 6%, 4% and 1%. A possible reason for much lower adsorption capacity for C-II4B-3 (besides the percentage of iron impregnated ~3%) might be problems with iron dispersion or penetration into the GAC material. RSSCTs and isotherms showed the same trend of effectiveness for As(V) removal by C-II4B-3 and A-3-7.

Figure 5.1 presents the relationship between iron content and adsorption capacity in isotherms (model solutions) and RSSCTs (groundwater) for Clemson University, Solmetex and ASU composites. Iron content of the media is plotted on the x-axis. Adsorption capacities (y-axis) are expressed as μgAs/mgFe) for an RSSCT effluent concentration (C_e) of 10 μg/L. Because arsenic adsorption to iron (hydr)oxides is the presumed mechanism for arsenic removal, it could be hypothesized that arsenic removal then be independent of iron content (x-axis). This does not appear to be the case. Therefore, it must be the iron mineral surface area, iron mineralogy, and/or blockage of pores by deposited iron as a function of depth into the Fe-GAC composite that influence arsenate adsorption capacity, and not only the iron content.

Figure 5.2 compares q values from batch and RSSCT experiments. The adsorption capacities (μgAs/mgFe) indicate that the Clemson University media had low values for both type of experiments. Solmetex media had better performance in batch experiments than in RSSCTs. Both ASU media had similar adsorption values in both studies with S-7-3 having the highest removal of arsenic.

EFFECTS OF PH AND ION COMPETITION

Evaluation of pH and ion competition influence was tested in isotherms. C-II4B-3 along with C-II9-8, C-IV13-6 and C-II14-2 were used for evaluation of pH effects in model solutions. C-II4B-3 was the best adsorbent for arsenate. As(V) adsorption capacities (q_o) were 0.12, 0.23, 0.007 and ~0.0002 (µg/mg)/(µg/L)$^{1/N}$ at pH levels of 5, 6.5, 7.5 and 9.0, respectively for C-II4B-3 (Chapter 3, Table 3.16).

The pH_{zpc} is the pH at which the adsorbent has a net zero surface charge (at pH < pH_{zpc}, the surface has a net positive charge; at pH > pHzpc, the surface has a net negative charge. Aqueous arsenate speciation is controlled by the pH dependent dissociation of two ionic species ($H_2AsO_4^- \leftrightarrow HAsO_4^{-2} + H^+$; pK_a = 7). With increasing pH, the net surface charge of the C-II4B-3 becomes less positive (i.e., decreasing attractive electrostatic force) until the pH_{zpc} (7.0) is surpassed. At pH > pH_{zpc}, the net surface charge is negative, producing a repulsive electrostatic force between $HAsO_4^{-2}$ and the adsorbent. This was demonstrated by the performance of GAC4 in this experiment, where there was better arsenate removal at lower pHs (5.0 and 6.5). Figure 5.3 presents a plot of adsorption capacities of the composites at their different pH_{ZPC}. The q_o values were obtained at C_e of 10 µg/L of As(V). This graph shows C-II4B-3 with similar capacities (~18 µgAs/mg-Fe) at low pHs (5.0 and 6.5), and decreasing capacities as the pH increases to 7.5 and 9.0.

Additional isotherms were used to test the influence of silicate and vanadate on arsenic removal. Modified NSFI-53 challenge water and C-4IIB-3 was used for this purpose. Arsenic adsorption by C-II4B-3 was diminished by 25% with silica present at 20 mg/L and pH=6.5. At pH=8.5 adsorption capacity of C-II4B-3 diminished by 80%. Silica competes with arsenate for surface adsorption sites in Fe-GAC materials and also decreases the surface charge, which results in greater electrostatic repulsion of arsenate. At the low vanadate concentrations tested, vanadate had only a small detrimental impact on arsenate adsorption in the NSFI-53 challenge water. As(V) adsorption capacities for the media were 0.22, 0.48, 0.25 and 0.52 µgAs/mg-adsorbent for waters at pH=8.5 and 100ppb of V, pH=6.5 and 100 ppb of V, pH= 8.5 without V , and pH= 6.5 without V, respectively.

MATERIAL PROPERTIES

Surface analyses by scanning electron microscope (SEM) coupled to an energy-dispersive X-ray spectrometer (EDX) were conducted on ASU samples. Figures 5.4 and 5.5 show graphs of these analyses. Both A-3-7 and A-J1-6 composites had a homogenous distribution of iron on the surface area of the GAC material. The X-axis represents a section of the material (line indicated on the photo) whereas the Y-axis displays energy counts.

In addition a cross-section analysis by SEM/EDX was conducted on A-J1-6. Figure 5.6 shows that most of the iron is deposited near the outer portions of the composite. Thus, it may be possible to improve arsenic removal through a slower deposition process which allows the iron to penetrate deeper into the GAC. Samples A-3-7 and S-4-11 had similar iron deposition treatment. Not enough mass of S-4-11 was available to perform cross section analysis this composite for comparison of iron distribution to the ASU samples.

Table 5.1 Isotherm parameters for different Fe-GAC composites in model waters, blended groundwater and surface water.

Manufacturer	Sample ID	Iron Content %	K	1/N	R^2	q_o at C_e 10ppb (µgAs/mgGAC) Dry basis	q_o at C_e 10ppb (µgAs/mgFe) Dry basis
Clemson University	C-II4-11	11.63	0.13	0.54	0.99	0.45	3.9
	C-II4B-3	3.4	0.07	0.55	0.99	0.25	7.3
	C-II9-8	7.9	0.09	0.55	0.94	0.32	4.1
	C-IV13-6	5.8	0.06	0.59	0.89	0.23	4.0
	C-II14-2	2.1	0.01	0.87	0.76	0.07	3.5
	C-II4B (GW)	3.4	0.0064	0.95	0.95	0.057	1.7
	C-II4B (Surface)	3.4	0.09	0.33	0.8	0.19	5.7
Solmetex	S-1-7	6.8	0.22	0.56	0.93	0.80	11.8
	S-2-4	3.8	0.18	-	-	-	-
	S-2B-11	11.2	0.032	1.19	0.92	0.50	4.4
	S-4-11	10.5	0.29	0.59	0.92	1.13	10.7
ASU	A-3-7	7.2	0.18	0.64	0.94	0.79	10.9
	A-J1-6	6.3	0.14	0.49	0.9	0.43	6.9
LLNL	L-294-1	1	0.01	0.8	0.96	0.063	6.3
As-SOC (Groundwater)							
ASU	A-3-7	7.2	0.09	0.61	0.99	0.37	5.13
Clemson University	C-II4B-3	3.4	0.02	0.86	0.72	0.14	4.11

Table 5.2 Calculated adsorption capacities for Fe-GAC composites evaluated in RSSCTs (* indicates experiments with spiked MTBE and benzene)

Media ID	**Initial As(V)**	**EBCT**	**pH**	**At Ce = 10 µgAs(V)/L**		**Complete As(V) Breakthrough**	
	(µg/L)	(min)		q (µgAs/mgGAC)	q (µgAs/mgFe)	q (µgAs/mgGAC)	q (µgAs/mgFe)
C-II4-11	33	2.5	7.83	0.009	0.08	0.039	0.34
C-II4B-3	26	4.0	7.01	0.065	1.91	0.097	2.85
C-II4B-3	26	10.0	7.01	0.089	2.62	0.110	3.24
C-III5-13	25	4.0	7.00	0.024	0.15	0.037	0.23
C-IV6-8	25	4.0	7.00	0.055	0.66	0.057	0.68
C-II9-8	33	2.5	7.83	0.009	0.11	0.021	0.27
C-IV11-7	25	4.0	7.00	0.053	0.71	0.062	0.83
C-1V13-6	33	2.5	7.83	--	--	0.021	0.36
C-II14-2	33	2.5	7.83	--	--	0.014	0.67
C-II4B-3	27	4.0	7.01	0.075	2.21	0.106	3.12
A-3	27	4.0	7.01	0.625	8.70	0.955	13.30
A-J1	27	4.0	7.01	0.459	7.29	0.707	11.23
L-294	27	4.0	7.01	0.060	8.00	0.125	16.67
S-1	25	4.0	7.00	0.230	3.40	0.321	4.75
S-1+2	25	10.0	7.01	0.318	4.43	0.375	5.22
C-II4B-3*	26	4.0	6.8-7.1	0.052	1.53	0.112	3.29
A-3*	26	4.0	6.8-7.05	0.352	4.90	0.409	5.70

Table 5.3 Summary of bed volumes treated during RSSCT ([a]Scottsdale groundwater blended with nanopure water; [b] spiked with MTBE and benzene)

Media ID	Initial As(V) (μg/L)	EBCT (min)	Water Matrix [a] (percentage groundwater)	pH	Bed Volumes Treated To Reach Effluent As(V) Concentration	
					Effluent As(V) = 10 μg/L	Effluent As(V) = 20 μg/L
C-II4-11	33	2.5	100%	7.83	1	20
C-II4B-3	26	2.5	33%	7.01	500	750
C-II4B-3	26	4.0	33%	7.01	4,000	7,600
C-II4B-3	26	10.0	33%	7.01	5,000	8,000
C-III5-13	25	4.0	33%	7.00	750	1,250
C-IV6-8	25	4.0	33%	7.00	1,500	2,500
C-II9-8	33	2.5	100%	7.83	700	900
C-IV11-7	25	4.0	100%	7.00	1,500	3,000
C-1V13-6	33	2.5	100%	7.83	10	100
C-II14-2	33	2.5	100%	7.83	1	20
C-II4B-3	27	4.0	33%	7.01	4,000	7,500
A-3	27	4.0	33%	7.01	39,000	75,000
A-J1	27	4.0	33%	7.01	25,000	49,000
L-294	27	4.0	33%	7.01	4,000	8,500
S-1	25	4.0	33%	7.00	20,000	>35,000
S-1+2	25	10.0	33%	7.01	15,000	30,000
C-II4B-3 [b]	26	4.0	33%	6.8-7.1	3,500	13,000
A-3 [b]	26	4.0	33%	6.8-7.05	23,000	>30,000

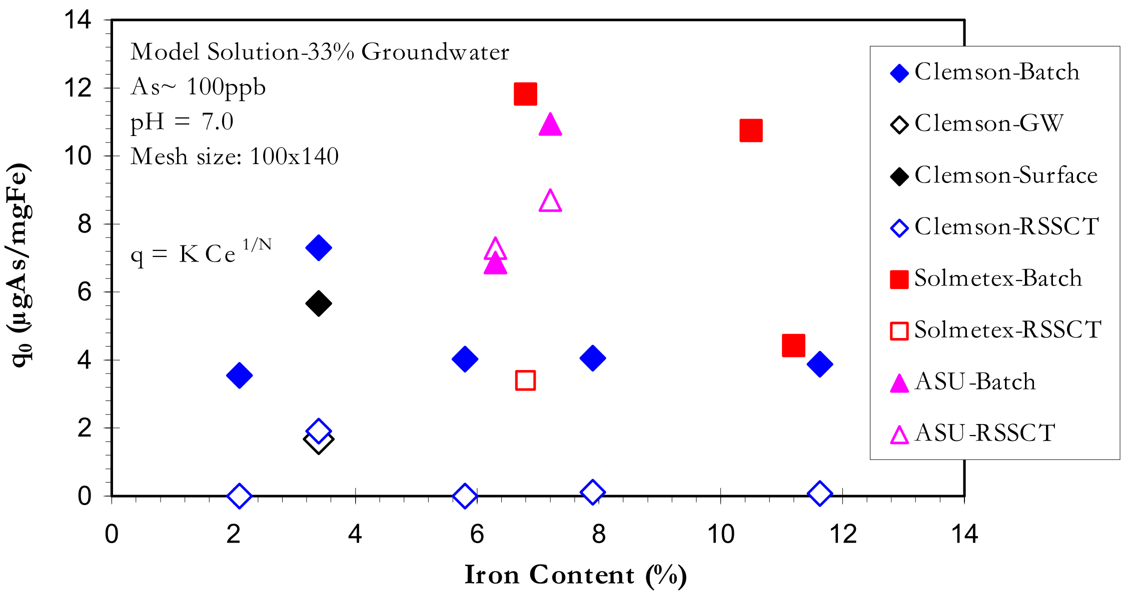


Figure 5.1 Media performance based on iron content for both RSSCT and batch tests. Scottsdale groundwater (33%) and model solutions were used for both studies respectively; test conditions were As(V) = 100 µg/L and pH = 7

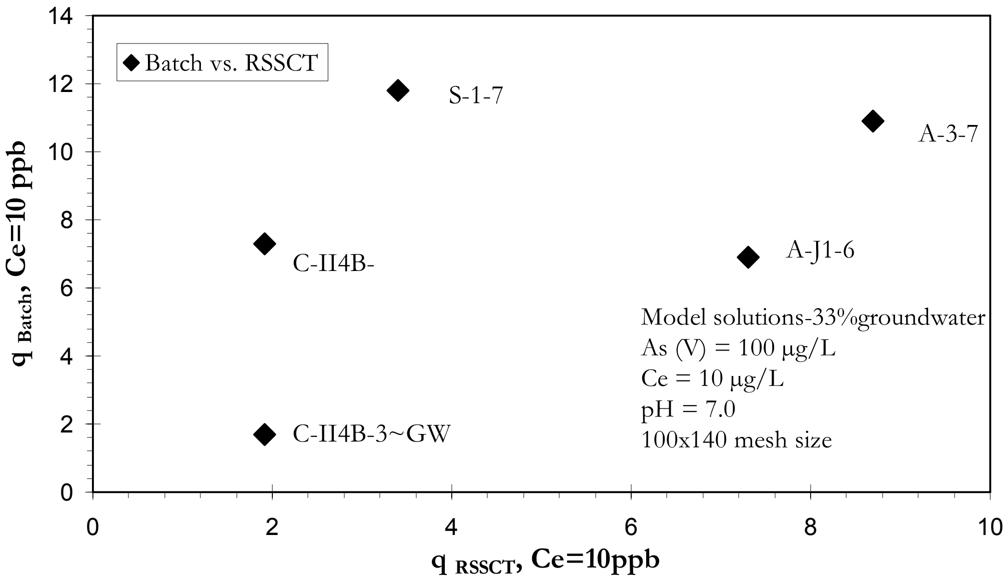


Figure 5.2 RSSCT vs. batch adsorption capacities for arsenic removal based on iron content

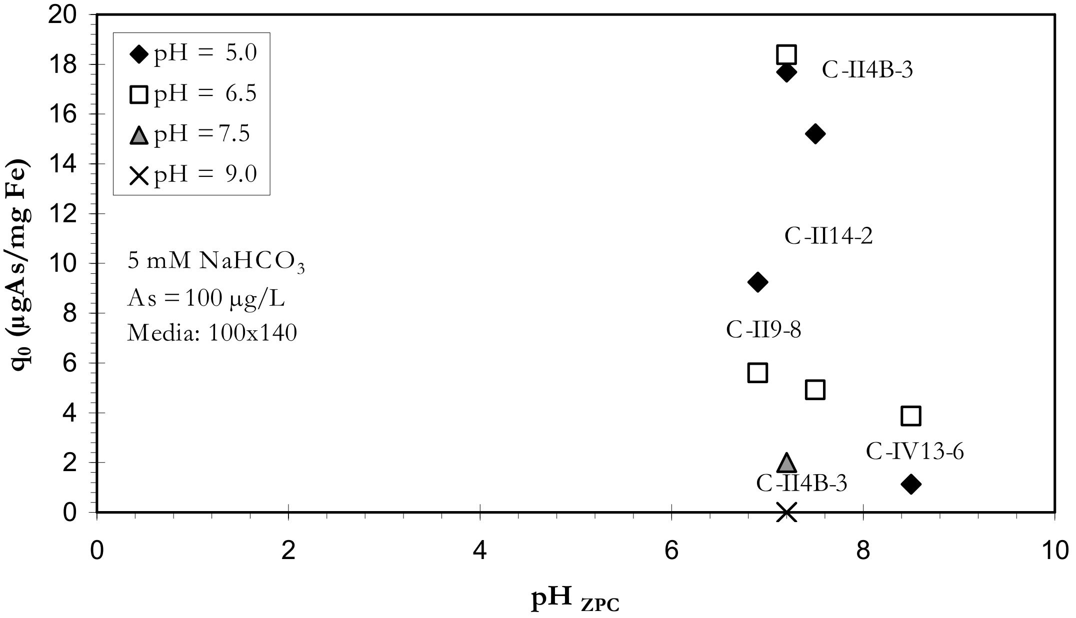


Figure 5.3 Batch adsorption capacities of media at different pH levels plotted vs. the pH of zero point charge of the composites.

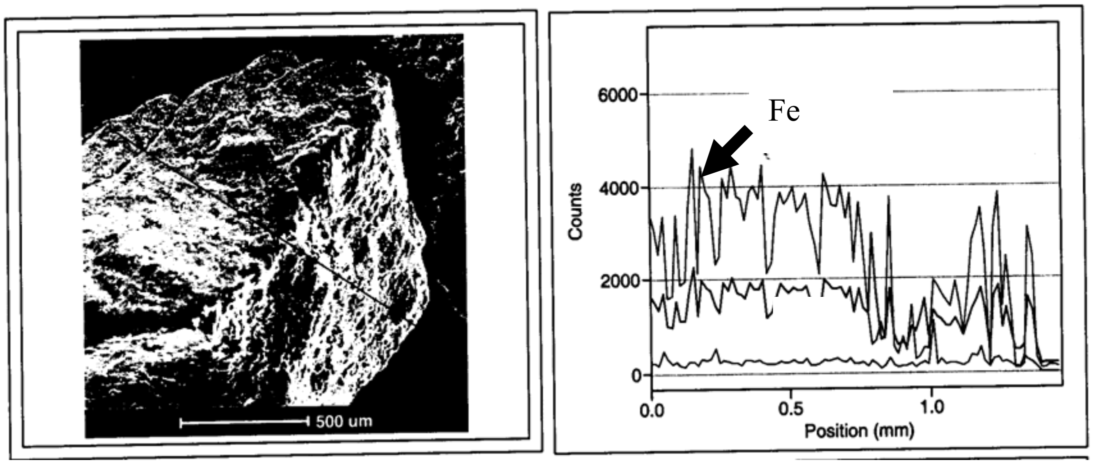


Figure 5.4 SEM/EDX surface analysis for A-3-7 (Norit HD3000 GAC)

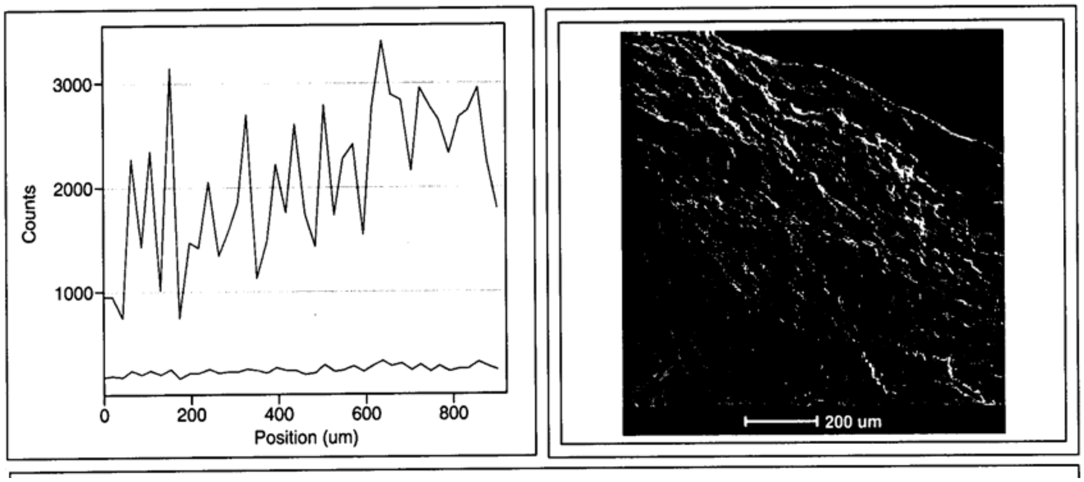


Figure 5.5 SEM/EDX surface analysis for A-J1-6 (Jacobi GAC)

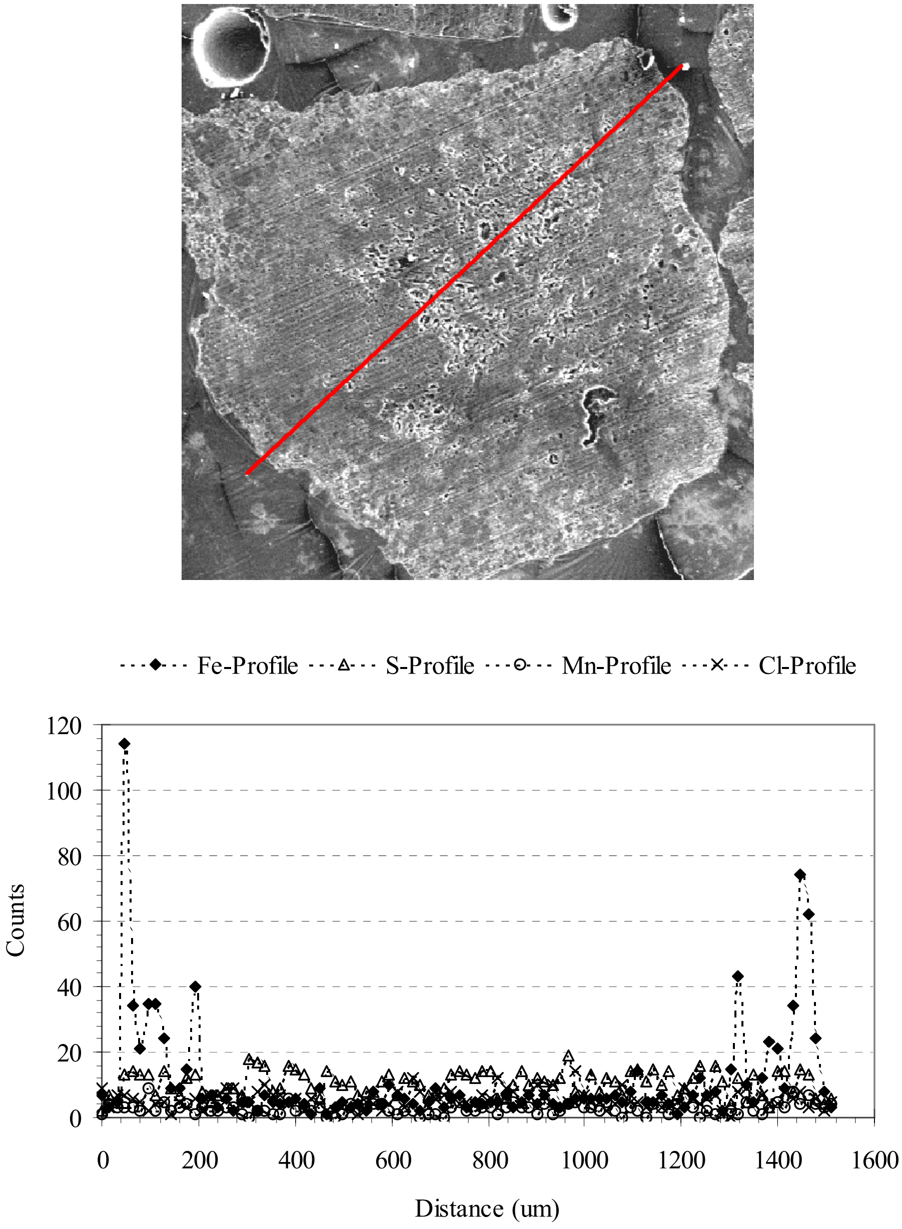


Figure 5.6 Elemental profile of cross-section through a Fe-GAC material (Jacobi)

CHAPTER 6 RECOMMENDATIONS FOR UTILITIES AND FUTURE RESEARCH

This project evaluated the "proof-of-concept" for using Fe-GAC composites as adsorbents for arsenic removal and organic contaminants. Batch adsorption experiments and column studies were conducted in different water sources to evaluate and identify the performance of Fe-GACs produced by Arizona State University, Clemson University, Solmetex Inc. and LLNL.

CONCLUSIONS

- Fe-GAC composite media contained <1% to 15% iron by dry weight. There were no friability issues during use of the media, nor did iron appear to "flake" off of the composite media. Thus Fe-GAC media appear suitable for batch or packed-bed use during water treatment.
- Arsenic removal by Fe-GAC composites depended highly upon the process used to impregnate iron. Iron-aerogel materials had the lowest iron content and exhibited the lowest arsenic adsorption capacities. Roughly six other techniques to impregnate iron into GAC were successful and were the focus of the study. For these materials iron impregnation did not alter the surface area significantly (<15% change), as measured by nitrogen deposition. However, arsenic adsorption varied significantly based upon the technique to impregnate iron.
- Arsenic adsorption was not a function of the iron content (i.e., mgFe/mgGAC). This implies that the technique to impregnate Fe-GAC composites and the resulting mineralogy and structure is probably more important than the iron content.
- The best performing Fe-GAC composite for As(V) from Clemson University (C-II4 and C-II4B) was produced via an iron hydroxide precipitation process. This was superior to iron impregnated via ion exchange, organic-ligand based, or zero valent iron based techniques. The zero valent iron based technique result achieved comparable or slightly better As(III) removal than other Clemson University Fe-GAC composites.
- The best overall performing Fe-GAC composite was synthesized by Arizona State University and Solmetex Inc. using a patented process. Generally, this process involves in-situ precipitation of iron (hydr)oxide using an oxidant and reduced iron species.
- Extensive media characterization was undertaken (surface area, pore size distributions, zeta potential, and various spectroscopy measurements). These proved valuable in assessing differences between iron deposition techniques.
- Batch kinetic experiments indicated that 100x140 mesh Fe-GAC composites reached pseudo-equilibrium for As(V) adsorption within 7 days of contact time. Adsorption isotherms were fit well by the Freundlich Isotherm model ($q = KC_e^{1/N}$).

- In batch experiments with Fe-GAC composites, As(V) adsorption improved as solution pH decreased. For example, the adsorptive capacity constant (K) decreased by a factor of ten for each full pH unit increase, between pH 5 and 9.
- In batch experiments with Fe-GAC composites and silicate (20 ppm) at pH 6.5 and 8.5, addition of silicate decreased As(V) adsorption at both pH levels. All Fe-GAC composites evaluated exhibited similar pH, silicate, vanadate and other competing ion effects.
- In batch and column experiments with Fe-GAC composites, As(V) adsorption was lower in groundwaters or NSFI-53 challenge water compared model solutions prepared from nanopure water at an equivalent pH as the groundwater. Thus, ions present in these more complex water matrices compete for arsenic adsorption sites on the Fe-GAC composite. Addition of 100 ppb vanadate to the NSFI-53 challenge water had almost no effect on As(V) removal. Addition of 20 ppm silicate to the NSFI-53 challenge water decreased As(V) adsorption at both pH 6.5 and 8.5, compared against the NSFI-53 challenge water prepared without silicate added. Thus silicate appears to be a major foulant/competitor for As(V) adsorption sites on Fe-GAC.
- In batch and column tests, decreasing the ionic strength of a groundwater through blending with nanopure water resulted in improved As(V) adsorption. These experiments maintained the same ratio of ions, but demonstrate that the concentration of competing ions affect As(V) adsorption.
- Rapid small scale column tests (RSSCTs) were conducted in continuous flow operation with empty bed contact times (EBCTs) of 2.5 to 10 minutes. Fe-GAC composites that performed best in batch testing, also had the best performance in RSSCTs. The ASU and Solmetex Inc. Fe-GAC composites achieved the longest run length (i.e., bed volumes treated). Lengthening the EBCT resulted in a larger number of bed volumes treated. The minimum EBCT recommended EBCT is 4 minutes; at 2.5 minute EBCT the mass transfer zone was not captured within the column.
- RSSCTs operated for 50,000 to over 100,000 bed volumes before complete As(V) breakthrough.
- RSSCTs were also conducted with a surface water containing dissolved organic carbon (DOC) and model groundwaters spiked with MTBE and benzene. Both waters also contained As(V). As(V) was removed effectively, and did not seem to be impacted by the presence of DOC, MTBE or benzene. Fe-GAC removed not only the As(V), presumably due to adsorption onto iron (hydr)oxides, but also removed the DOC and synthetic organic chemicals (MTBE and benzene). Organics were presumably removed by adsorption onto the GAC. Therefore, iron impregnation does not appear to hinder organic removal by GAC, but adds the capability to remove arsenic.
- GAC is a relatively inexpensive substrate to impregnate with iron. For water treatment situations were co-removal of arsenic and other contaminants suitable for removal by GAC is desired (e.g., SOCs, radionuclides, DOC) Fe-GAC composites are a feasible option.

RECOMMENDATIONS FOR FUTURE RESEARCH

- Optimization of the selection of base GAC substrate and iron deposition process needs to be conducted. This should follow the basic technique which resulted in the best performing Fe-GAC composites (produced by ASU and Solmetex Inc.).
- Batch equilibrium tests proved to be excellent indicators of more labor-intensive RSSCT performance. Future work should use batch tests to screen new composites. However, optimization of Fe-GAC composites must also consider that deeper iron penetration into the GAC base material may impact arsenate mass transfer. Therefore, RSSCTs should continue to be conducted to assess mass transport limitations.
- Because Fe-GAC composites are new materials, there is a need to compare arsenic breakthrough achieved from pilot tests against those achieved by RSSCTs to validate the scaling approach.
- Improved spectroscopic analysis of Fe-GAC composites is warranted to understand the nano-structure of the iron deposits (coated surface versus crystals crossing through the pore space). This could help optimize the iron deposition process (e.g., duration of iron treatment). Ultimately the goal should be to maximize iron content for the best iron mineralogy to result in the most arsenic removal.
- Forensic analysis of spent media would provide additional insight into the role of foulants and changes in mineralogy over time.
- A detailed economic analysis of iron-oxide impregnated GAC composites should be conducted. Without full-scale production of these products the economic analysis could be conducted based upon costs of raw materials, costs for similar processes applied for other products, and lifecycle cost of the media.

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APPENDIX A –ISOTHERMS FOR COMPARISON OF FE-GAC COMPLETED AFTER COMPOSITE SELECTION FOR RSSCTS

After the completion of batch and column tests presented in Chapters 3, 4, and 5 new Fe-GAC composites continued to be produced in an attempt to optimize their properties to maximize As(V) removal. Two batches of Fe-GAC composites were produced and evaluated in batch experiments for As(V) removal.

Figure A-1 summarizes the isotherms obtained for Fe-GAC composites prepared by Clemson University following a similar approach as employed for C-II4B-3. The results indicate a slight improvement in As(V) removal occurred for two of the new materials (C-II4C-3 and C-II4C-4). However, when these two new materials were compared against materials synthesized using the oxidant/ferrous process employed at ASU and Solmetex Inc., the sample C-II4C-3 and C-II4C-4 had >50% less As(V) capacity of the best performing materials (A-3B or S-4) (Figure A-2). A-3B-11 and S-4-11 composites were prepared with the same approach for iron deposition and contain similar iron content (11%Fe and 10%Fe, respectively).

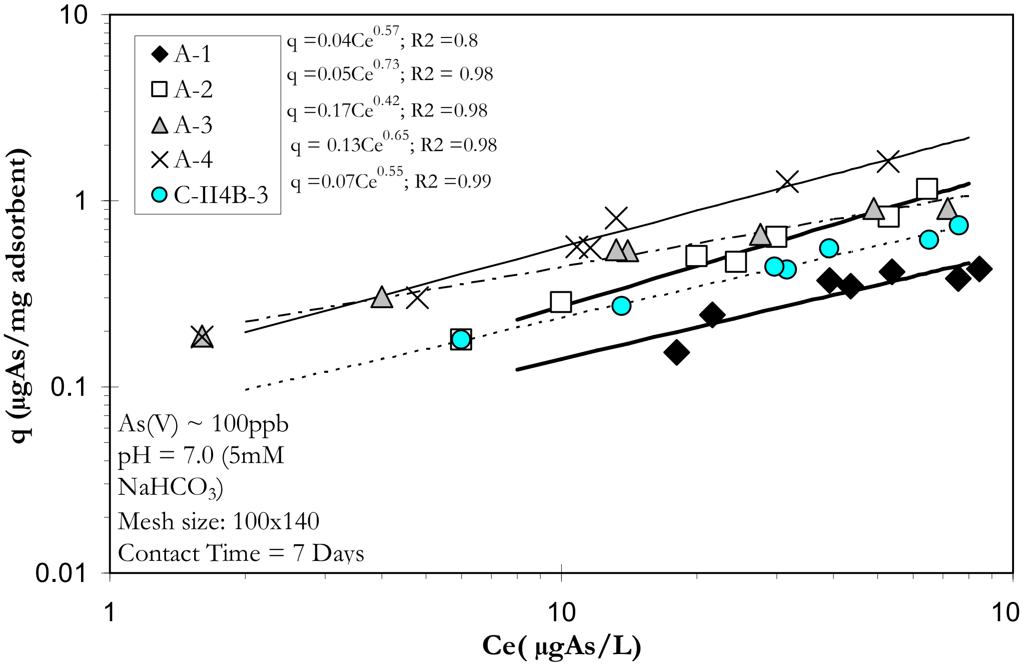

Figure A-1 Isotherm test in model solution for arsenate removal showing 4 new versions of C-II4B in parallel with old version. These new media were prepared by iron hydroxide precipitation and have same iron content than C-II4B-3.

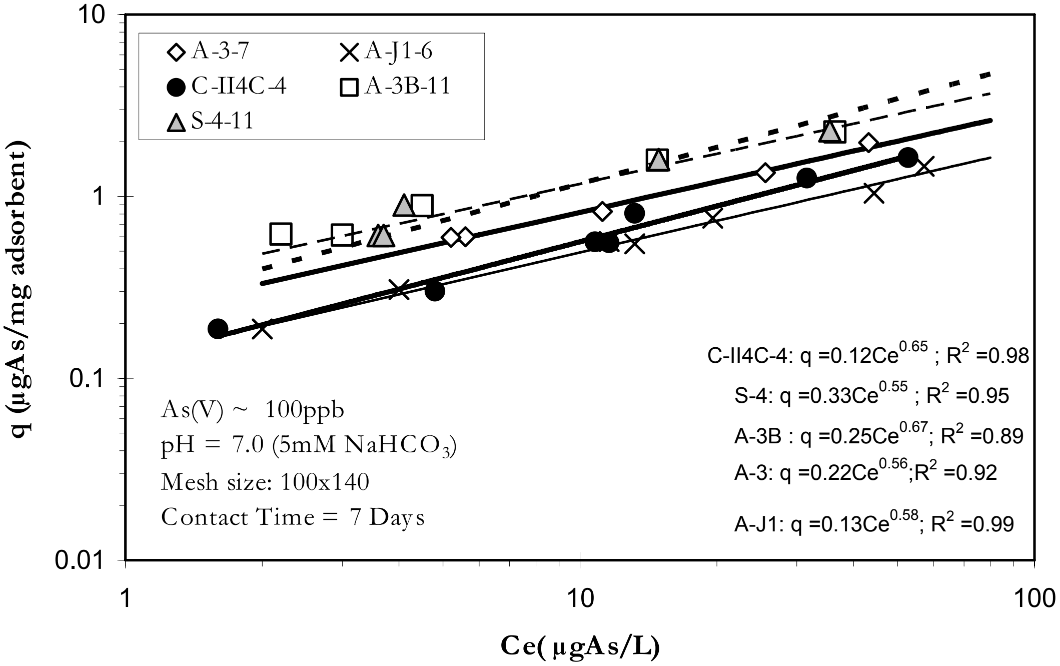

Figure A-2 Isotherm test in model solution using Fe-GACs from ASU, Solmetex and Clemson University. October 2005

ABBREVIATIONS

As(III)	Arsenite
As(V)	Arsenate
ASU	Arizona State University
AZ	Arizona
BV	Bed volume
DOC	Dissolved organic carbon
$EBCT_{LC}$	Empty bed contact time of large scale column
$EBCT_{SC}$	Empty bed contact time of RSSCT column
Fe	Iron
Fe-GAC	Iron (hydr)oxide impregnated granular activated carbon
ft	Foot
g	gram
GAC	Granular activated carbon
GC	Gas chromatography
GFAA	Graphite furnace atomic absorption spectroscopy
gpm	Gallons per minute
GW	Groundwater
K	Freundlich isotherm adsorption coefficient
L	Liter
LLNL	Lawerence Livermore National Lab
M	Meter
mL	Milliliter
MTBE	Methyl *tert*-butyl ether
NSFI	National Sanitation Foundation International
pH_{ZPC}	pH of zero point of charge
ppb	parts per billion
ppm	parts per million
q	Adsorption capacity
RSSCT	Rapid small scale column test

SEM	Scanning electron microscopy
Si	Silica
SOC	Synthetic organic chemical
TM	Trademark
UVA254	Ultraviolet absorbance at 254 nm
V	Vanadate
VOC	Volatile organic chemical