SYNTHESIS AND CHARACTERIZATION OF A NANOPARTICLE-ENHANCED FILTER MEDIUM FOR DECENTRALIZED WATER PURIFICATION SYSTEMS

by

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Engineers and scientists are problem solvers. Whether it is basic research or commercialization of a prototype, intellectual challenges and the satisfaction of research have been keen motivators for me, driving my academic pursuits in both undergraduate and graduate engineering. Newark, Delaware has been like a second home for me during these past six years. Having received both my Bachelor's and Master's degrees in Civil and Environmental Engineering at the University of Delaware, I am thankful for the technical and analytical knowledge and skills I developed within those programs, and the many collaborative connections I have experienced with fellow students and faculty. I would like to thank Professor Daniel Cha, who first offered me a position under the environmental engineering program at the University of Delaware my junior year, which led to my evolving interest in the applied engineering interdisciplinary concentration of environmental engineering.

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ABSTRACT

A synthesis procedure was developed to generate a tailored point of use (POU) filter medium that incorporates nanoscale zero-valent iron (nZVI) and granular activated carbon (GAC) for the enhanced treatment of drinking water. Several characterization techniques were employed to evaluate the efficiency of the synthesis procedure and the generated product itself. First, iron quantification via nitric acid extraction illustrated that at low iron loadings transfer of iron onto GAC was efficient and complete, and that negligible iron loss occurred post calcination during either sieving or reduction. Second, Brunauer, Emmett, and Teller (BET) specific surface area measurements for the virgin-GAC and nZVI-GAC were determined to be 798 $m^2 \cdot g^{-1}$ and 792 $m^2 \cdot g^{-1}$ respectively, indicating a negligible decrease in GAC surface area post synthesis. Third, scanning electron microscopy (SEM) imagery and energydispersive X-ray spectroscopy (EDS) measurements confirmed the presence and general surface distribution of iron nanoparticles on GAC. Finally, X-ray diffraction (XRD) intensity patterns confirmed the presence of ZVI on the surface of GAC and that the synthesis procedure successfully reduced ferric iron to its zero-valent state. To simulate drinking water contaminated with enteric microorganisms, two bacteriophages MS2 and $\phi X174$ were used as surrogates. A series of batch tests were performed to measure removal efficiencies for each bacteriophage over different time intervals. Varying degrees of removal were observed for each bacteriophage. Experimental results showed that the nZVI-GAC filter medium demonstrated greater removal efficiency for MS2 compared to virgin-GAC. The first-order rate coefficients

for MS2 removal by virgin-GAC and nZVI-GAC were determined to be 0.037 and 0.0961 PFU·min⁻¹, respectively. However, performance for ϕ X174 removal appeared to be similar between both the control and nZVI filter medium. The first-order rate coefficients for ϕ X174 removal by virgin-GAC and nZVI-GAC were 0.0298 and 0.0413 PFU·min⁻¹, respectively. The varying effect on MS2 removal was also observed by adjusting the percent weight of iron coated on the GAC surface. The experimental results from the varied percent iron loading tests identified a rate-limited removal capacity for nZVI. Removal mechanisms were then suggested to explain the observed experimental data. Finally, drawing on conclusions from the observed experimental data, the potential application for such a nanoparticle-enhanced POU filter medium was explored. Ultimately, the engineered application of nZVI-GAC was suggested as a substitute for the conventional in-the-field POU technologies.

Chapter 1

INTRODUCTION

The identified persistence of waterborne pathogens continues to threaten the health and safety of the public in both industrialized and developing nations. In the United States, three categories of waterborne human enteric organisms of the greatest consequence in producing disease are bacteria, viruses, and amoebic cysts. Typical waterborne bacterial diseases are typhoid, cholera, paratyphoid, and bacillary dysentery. Diseases caused by waterborne viruses include poliomyelitis and infectious hepatitis. Such waterborne pathogens are commonly found in water sources due to the presence of fecal matter from sewage discharges, leaking septic tanks, and runoff from animal feedlots [1]. In the field of municipal water treatment, disinfection is most commonly accomplished through the use of chemical and physical agents. In applying the disinfection agents or means that have been described, the following factors must be considered: contact time, concentration and type of chemical agent, intensity and nature of physical agent, temperature, number of organisms, types of organisms, and the nature of suspending liquid. Currently, chlorine is most widely used for the disinfection of microbial pathogens due to its high oxidization potential. Typically, the solid form of chlorine (calcium hypochlorite) is used for onsite treatment, which when added to water forms hypochlorous acid and calcium hydroxide. With the

resulting pH increase, such conditions favor the formation of the hypochlorite species (OCI; $pk_a = 7.3$) [2]. Although the U.S. Environmental Protection Agency (EPA) classifies pH as a non-mandated secondary contaminant, state reported secondary maximum contaminant levels for the pH of drinking water range from 6.5 to 8.5 [3]. Therefore, under typical drinking water conditions hypochlorite exists as the dominating free chlorine species and, given that free chlorine is thermodynamically unstable, when present in water it will react with the various reduced compounds in the source water which can include sulfide, heavy metals, organic matter, and ammonia. The various complex reactions which proceed then result in the formation of various combined chlorine (chloramines) and chloro-organics, some of which are known to be highly toxic and carcinogenic to organisms. Although the use of chlorine as a disinfectant effectively mitigates microbial contamination, its use as a disinfectant also produces a number of undesired byproducts. Concerns surrounding the formation of disinfection byproducts (DBP) arise from reported studies which identify certain DBPs as a potential health risk to public drinking water consumers. The composition of the source water and disinfectant used ultimately determines the formation of specific DBPs. However, given the favorable use of chlorine as a disinfectant for microbial contamination, current governmental health and safety regulations only address chlorinated DBPs and seem to overlook the remaining, potentially more toxic, DBPs. Given the seemingly overwhelming number of total DBPs in combination with sparse governmental regulation and limited innovative research into understanding

DBP effects and behavior, the full impact that DBPs will have on the public in regards to chronic exposure to DBP-contaminated drinking water is currently unclear.

To address the immediate public concerns associated with chlorination (i.e., taste and odor), decentralized treatment options have been developed to serve as point of use (POU) treatment of supplied municipal drinking water. Typically, the current POU treatment systems used for treating municipal drinking water incorporate a blend of reactive media, distinct from each other with regards to their affinity towards various waterborne constituents. Commonly found in POU drinking water treatment systems, granular activated carbon (GAC) is widely used as a reactive catalyst for removing organic and inorganic constituents from water. GAC's impressively large surface area, electropositive surface, and highly porous structure makes it ideal for removing constituents that are attracted to its vast number of sorption sites per weight basis. In conjunction with GAC, various ion exchange resins are also incorporated alongside in POU drinking water treatment systems. The ion exchange treatment process uses special resins to remove charged, inorganic contaminants like copper, lead, arsenic, chromium, nitrate, uranium, and excess fluoride from water. Each exchange resin has a unique number of mobile ion sites that translate to a set quantity of exchanges per unit of resin. When source water passes over the surface of the resin bead, it exchanges the charged contaminants present in the water for the charged ions stored on the resin surface, storing the attracted constituents on its surface.

In regards to municipal drinking water, an estimated 88 to 100 million persons in the United States are served by community drinking water systems that rely on groundwater as their sole or primary source [4]. Withdrawals of groundwater in the United States increased from 26 to more than 75 billion gal/day from 1950 to 1995 [5]. Of all the water used in the United States, in the year 2000 about 21 percent (roughly 408 billion gallons per day) came from groundwater sources. Water from surface water sources accounted for the remaining 79 percent [6]. Growing concerns for using groundwater as a drinking water source arise when dealing with DBPs. As previously mentioned, a large number of DBPs are not regulated even though they are suggested to be more toxic than chlorinated-DBPs; these include the brominated-DBPs. Due to the high solubility of bromide ions, bromine is more commonly detected in groundwater than in surface water, especially considering groundwater sources in coastal regions where tidal flux permits interaction between groundwater and seawater.

Permeable reactive barriers (PRB) are a passive, in situ technology commonly incorporated at Superfund and Brownfield sites to remediate contaminated groundwater. Since their first commercial application in Sunnyvale, California in November 1994, the use of iron-based PRBs has evolved from innovative to the accepted standard practice for groundwater remediation [7]. Worldwide, there have been nearly 120 applications of iron-based PRBs, 83 of which are considered full scale. In the United States, there have been more than 90 applications of iron-based

PRBs, 67 of which are full scale [8]. Zero-valent iron (ZVI) is the most common reactive media used for abiotic reduction in PRBs due to its ability to treat a variety of organics, heavy metals, and radionuclides. It is widely used not only for its effective reactive affinity towards various constituents, but also because it is a relatively inexpensive technology when compared to alternative reactive media.

In a 2005 published study, ZVI was assessed as to its effectiveness at removing and inactivating waterborne viruses and was suggested as an alternative or complimentary means to water and wastewater treatment [9]. A number of studies have shown that iron oxides can remove and inactivate viruses in water [10-13]. Although the mechanism for the removal and inactivation is not fully understood, the process has been suggested to involve adsorption of virus particles to iron oxide species through electrostatic attraction [10, 14]. This is then followed by inactivation of adsorbed viruses due to the strong attachment force, which causes the viruses to undergo lysis or become noninfectious [10, 11]. These studies suggest an intriguing possibility that zero-valent iron may continuously remove and inactivate viruses in water through corrosion and formation of complex oxides at the iron surface. The 2005 study successfully demonstrated, using commercial Peerless iron, the efficacy of zero-valent iron and virus inactivation.

The focus of this study was to develop and demonstrate an innovative and cost-effective in situ technology for improving the removal efficiency of waterborne pathogens using current POU drinking water treatment systems. This enhanced

removal performance was achieved by incorporating nanoscale ZVI (nZVI) onto the surface of a common commercially used POU filter medium, GAC.

Chapter 2 LITERATURE REVIEW

2.1 Permeable Reactive Barrier (PRB), Reactive Media, and Mechanisms

The concept of PRBs to treat contaminated groundwater is straightforward. A contaminant-specific reactive material is placed in the saturated subsurface to intercept a contaminated plume as it travels with the natural gradient. As the contaminant moves through the designated reactive media, physical and chemical processes transform the hazardous contaminant rendering it either immobile or mineralized. PRBs are a passive, in situ technology with a high potential to treat shallow aquifers at a lesser cost than the traditional pump-and-treat methods [15].

A common groundwater constituent often addressed by the employment of a PRB at contaminated groundwater sites is uranium. Uranium contamination of groundwater has been detected at numerous sites worldwide, reflective of uranium's historically high production rate. In the United States, uranium contaminated sites are primarily associated with U.S. Department of Energy (DOE) nuclear weapons manufacturing areas, and mine tailing sites for uranium ores [16]. Most mines that produced uranium as a primary commodity are, or were, located in Colorado, Utah, Wyoming, New Mexico, and Arizona, typically on Federal and tribal lands. The

number of sites associated with uranium, as identified in the EPA database, is roughly 15,000. Of these uranium sites, more than 4,000 are mines having documented production [16]. Exposure to ionizing radiation from uranium causes acute or chronic health effects. Effects from acute exposure to high levels of the released radiation include hair loss, skin burns, gastrointestinal distress, and death. Chronic effects are primarily cancer related. Once uranium, or any radionuclide, is ingested it is distributed through the body to different organs, remaining present for days to years until it decays or is excreted. In the case of uranium, however, any ingestion of the uranium isotopes will significantly affect bone, muscles, and the kidneys, as target organisms [17]. So, needless to say, uranium is considered a problematic groundwater contaminant and, therefore, will be briefly used as an example for treatment purposes involving PRBs and ZVI.

Since the first commercial PRB application was installed in Sunnyvale, California in November 1994, the use of iron-based PRBs has evolved from innovative to the accepted standard practice for groundwater remediation [7]. As previously mentioned, ZVI is the most common media used for abiotic reduction in PRBs due to its ability to treat a variety of organics, heavy metals, and radionuclides. Reactive media such as carbon sources (compost), limestone, granular activated carbon, zeolites, ion exchange resins, sulfate reducing bacteria, and others have also been deployed in recent years to treat heavy metals and various organic compounds [8]. ZVI is widely used not only for its effective reactive affinity towards various waterborne constituents, but also because it is a relatively inexpensive media in comparison to several alternative reactive media. However, issues do seem to arise with ZVI-based PRBs due to its high redox-sensitivity towards groundwater constituents, which will often affect removal performance and PRB longevity. However, preliminary studies using long-term column tests to evaluate the longevity of PRB systems suggest that, after installation, decades could pass before PRBs will lose reactivity [8]. Depending on site-specific conditions, ZVI PRBs are now expected to last 10 to 30 or more years before reactivity or hydraulic issues will result in the need for maintenance [8].

Although the chemical mechanisms responsible for uranium uptake by ZVI are not fully understood, abiotic reductive precipitation is the likely scenario. In carbonate-dominated groundwater with moderate pH, abiotic reductive precipitation of a uranyl-carbonate complex (the main component of uranium in mine tailing seepage) proceeds to uraninite. However, chemical mechanisms other than reductive precipitation have also been suggested for the uptake of uranium by ZVI. It has been suggested that the predominant uranium removal mechanism is adsorption to the ferric oxides and oxyhydroxides species, which make up the passivation layer that forms during the oxidation of ZVI [18]. It should be noted that this adsorption mechanism is not unique to uranium isotopes. Extensive laboratory testing and actual in situ field applications that use ferric oxides for adsorbing heavy metal, various solvents, waterborne pathogens, and radionuclide contaminants from ground and drinking water have been examined. Results conclude that efficient contaminant removal can be achieved through the use of ferric oxides in combination with highly electron-rich ZVI cores.

2.2 ZVI Structure and Composition

Particle shape, size and composition are important properties that affect the intrinsic and physical properties of nanoparticles. For ZVI, there are many variations on its exact use for the removal of contaminants from soil and water. ZVI incorporated into PRB design is predominantly done so in the form of granular, amorphous cast iron tailings. However, regarding the variations for ZVI usage, it has also been incorporated into groundwater systems in the form of nanoscale ZVI which in recent years has led to increased attention for its potential use in various engineering applications. There are two potential advantages of using nanoparticle ZVI over the granular form: (1) nanoparticles can be delivered to deep subsurface contaminated zones in a less destructive manner than excavation and placement of its granular form, and (2) due to the greater surface area to mass ratio of iron nanoparticles, potentially nanoparticle ZVI may be more effective at degrading some contaminants [19]. However, there are several fundamental issues regarding the use of iron nanoparticles which include the mobility of nanoparticles in subsurface zones under various conditions and the limited understanding behind the kinetics and degradation byproducts associated with ZVI. In particular, the long term persistence of the

reactivity of ZVI nanoparticles is of most concern, which becomes very important when designing treatment systems to target specific contaminants.

In examining the structure of metallic iron (ZVI) it is important to note that it is thermodynamically unstable under ambient or aerobic conditions. If metallic iron is taken immediately from its fundamental ground state to aerobic conditions, it exhibits an exothermic reaction occurring as the electron-rich ZVI core interacts with the electron acceptor oxygen naturally present in the air composition. Therefore, given such a reaction, ZVI cores will always posses a thin protective iron oxide film consisting of FeO, Fe₃O₄, and Fe₂O₃ under aerobic conditions. The exact thickness and percent composition of these iron oxides present over the ZVI core depends specifically on the manner in which the core is exposed to oxidizing conditions. Typically, these thin oxide layers range only a few nanometers in thickness. Altogether, the oxide layers protecting the ZVI core can be practically viewed as an inherent part of the nanoparticle [20]. In order to evaluate the specific structure of synthetically prepared ZVI particles with regards to the composition of the outer iron oxide shell or determining the redox state of iron, certain characterization practices need to be employed which include transmission electron microscopy (TEM), scanning electron microscope imagery (SEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD).

2.3 Synthesis of Carbon-supported Nanoscale ZVI (nZVI)

As previously mentioned, granular activate carbon (GAC) is widely incorporated in POU drinking water treatment systems for removing contaminants. In recent years, several publish studies have presented the idea of incorporating iron nanoparticles onto the surface of selective catalysts [21-25]. Particular attention around selective catalysts has focused heavily on the use of various forms of carbonbased materials as support structure for iron nanoparticles. In these studies, the reasoning behind incorporating nanoscale ZVI (nZVI) with a carbon-based media stemmed from observing iron's effectiveness at remediating contaminated groundwater sites when incorporated into PRB designs in granular form. As previously mentioned, one of the advantages of using nanoparticles in groundwater remediation systems is the in situ potential of being able to simply inject it into subsurface locations.

Methods for coating iron onto the surface of carbon particles primarily involve the use of various ferric and ferrous salts followed by either chemical or thermal reduction of iron to reach its zero valent state. Commonly reported procedures for coating iron onto various carbon-based materials for groundwater applications generate coated products with high iron yields (15-40 %wt.), primarily relying on adsorption-only mechanisms forced to act under acidic conditions. The carbon-based materials used for coating purposes vary in particle size, particle shape, particle density, and specific surface area. Examples of carbon-based materials used include

fullerene or carbon nanotubes which can have a particle diameter of 12 nm, carbon black which can have a particle diameter of 42 nm, along with micron size powder activated carbon and granular activated carbon.

As stated, the reduction of the adsorbed ferrous and ferric salts on the carbon surface can be performed using several methods. Commonly reported is the use of sodium borohydride (NaBH₄) as a primary reducing agent. Used under anaerobic conditions, it reacts with water to evolve hydrogen and sodium hydroxide. Supplied heat decomposes it to release hydrogen gas which then reacts with the adsorbed transition metal catalysts, in this case iron, to liberate the bonded hydrogen. The resulting product is metallic iron. In addition to a wet-chemistry approach, reduction of iron oxides can also be carried out at very high temperature under anoxic conditions [21]. According to the published literature, there are currently two major thermal-anoxic processes for the reduction of carbon-supported iron oxides to metallic iron. The first of the published reduction procedures involves the use of an inert gas (nitrogen) to create the anoxic atmosphere in closed system in combination with a 3 hour reduction time at 800 °C [21]. The second more commonly used reduction procedure involves using hydrogen to develop the anoxic atmosphere. The benefit of using hydrogen as opposed to nitrogen is that hydrogen is an excellent reducing agent and therefore, reduction of iron can be achieved using much lower temperatures (475-600°C) during a shorter period of time. However, there are greater safety issues to consider when performing reduction processes at extreme temperature using hydrogen

as the reducing agent. The possibility for a violent reaction (i.e., an explosion) can occur given the proper conditions or faulty system design. As it turns out, industry has adopted the use of hydrogen as a reducing agent for commercialized production of iron oxide nanoparticles. The Japanese company Toda Kogyo, for example, is widely recognized as a leading producer of ZVI and iron nanoparticles generated using a thermal-hydrogen reduction procedure for various remediation applications [21]. Although the incorporation of ZVI onto carbon catalysts is not exactly a new technology, its engineering application is more or less confined to specific use in groundwater remediation of chlorinated organic solvents and heavy metals, some of which include hexavalent chromium and arsenic [21-25]. Recently, there has been no extensive research published that addresses further application of carbon-supported ZVI media, and few tailored synthesis procedures exist in the literature.

2.4 Disinfection of Viruses in Drinking Water

The primary purpose of the disinfection process in drinking water treatment is the control of waterborne diseases through inactivation of any pathogenic microorganisms present in the water [26]. Disinfection refers to the selective destruction of disease-causing organisms. All of the organisms are not destroyed during disinfection process. This differentiates disinfection from sterilization, which is the destruction of all organisms [27]. In the United States, three categories of waterborne human enteric organisms of the greatest consequence in producing disease

are bacteria, viruses, and amoebic cysts. Microbiological monitoring for fecal indicator bacteria, i.e., *Escherichia coli*, in drinking water continues to serve as a common practice in managing the safety and quality of drinking water. However, not all microbial agents are monitored and quantified at treatment facilities due to the high costs associated with such continuous and extensive microbial evaluation. Therefore, there is always some level of uncertainty associated with the exact composition of processed drinking water and the possible presence of microorganisms due to a lack of efficient contact time between disinfecting agents and the organisms. In the field of municipal drinking water treatment, disinfection is most commonly accomplished through the use of chemical and physical agents.

Chemical agents that have been used as disinfectants include (1) phenol and phenol-compounds, (2) alcohols, (3) iodine, (4) chlorine and its compounds, (5) bromine, (6) ozone, (7) heavy metals and related compounds, (8) soaps and synthetic detergents, and (9) hydrogen peroxide [27]. Out of the listed chemical agents, chlorine and its compounds are most widely used for the disinfection of microbial organisms due to the high oxidization potential.

Physical disinfectants that can be used include heat, light, radiation, and sound. Heating water to its boiling point, for example, will destroy the major diseaseproducing, non-spore-forming bacteria. Sunlight is also a good disinfectant. Ultraviolet radiation in particular is a good disinfectant that can successfully sterilize small quantities of water. The efficiency of the process depends on the penetration of the rays into water. The contact geometry between the UV-light source and the water is extremely important, because suspended matter, dissolved organic molecules, and water itself will absorb the radiation, in addition to the microorganisms. Sound can also be used, but it needs to be done so continuously to prevent microbial reproduction.

In applying the disinfection agents or means that have been described, the following factors must be considered: contact time, concentration and type of chemical agent, intensity and nature of physical agent, temperature, number of organisms, types of organisms, and the nature of suspending liquid [27]. Disinfection of microorganisms usually results from the blighting of the cellular structure which can cause changes in cell permeability and enzyme activity. Ultimately, such disturbances in cell activity prevent microorganisms from being able to multiply causing them to die off.

2.5 GAC Potential for Removing Microorganisms from Drinking Water

GAC functions by adsorption or adhesion. In POU drinking water treatment systems, organic molecules are drawn to the surface of the GAC and are held by a molecular attraction. The forces that attract the organic molecules and pull them out of solution must be stronger than the forces that are keeping them in solution [28]. It has been reported that in addition to organic constituent removal, GAC has also been observed to be capable of removing various microorganisms from water through

adsorption mechanisms [29-31]. Virus adsorption is strictly a surface reaction. Therefore, with carbon-based materials of similar surface reactivity, the percentage of removed viruses should increase as surface area increases. Also, the finer the mesh unit of GAC used the higher the available surface area there is on a weight basis. In Hijnen (2010), they evaluated GAC capacity for adsorbing several microorganisms: MS2, E. coli, spores of C. bifermentans as indicators for pathogens, and (oo)cysts of C. parvum and G. lamblia [31]. The measured results from the batch experiments demonstrated that cysts could be significantly removed from solution (1-2 log units). This removal was concluded to be largely attributed to attachment or adsorption of the organisms onto the charged GAC surface. However, they observed no removal of MS2 and limited removal of the indicator bacteria. Interestingly, in Powell (2002) MS2 removal was observed in batch tests using GAC (10x40 mesh) and an activated carbon fiber composite (ACFC) [30]. It was observed that although removal occurred using both carbon types, the viruses displayed a wide range of adsorption behavior depending on the type of carbon evaluated. It should also be noted that higher adsorption removal may have been observed in this study due to the lengthy 3-hour contact time used for the batch experiments as opposed to a simple flow through system as used in Hijnen (2010).

2.6 ZVI Potential for Removing Microorganisms from Drinking Water

In a 2005 published study, ZVI was assessed as to its effectiveness at removing and inactivating waterborne viruses and was suggested as an alternative or complimentary means to water and wastewater treatment [9]. A number of studies have shown that metal oxides can remove and inactivate viruses in water [10-13]. In Sagripanti (1993) the inactivation of five surrogate viruses of different biochemical and structural compositions could be inactivated by copper(II) or iron(III) alone over a 30-minute period in a concentration-dependent fashion [12]. In Chu (2003), $\varphi X174$ and MS2 were used to simulate virus transport through porous media to drinking water wells in natural systems [13]. The results showed that the extent of water content had an effect on inactivation but mostly that the presence of in situ metal oxides was the significant factor responsible for virus adsorption and inactivation. Their results confirmed the PRB potential of using metal oxides as hydrological barriers in preventing microbial contamination in the subsurface environments. In Ryan (2002), the order of the proposed reaction kinetics pertaining to surface inactivation of viruses occurs as such: (1) the attachment of to ferric oxyhydroxide patches, favored by electrostatic attraction; (2) inactivation at the surface, caused by the strong attachment force; and (3) release of noninfectious, disintegrated viruses to solution [10]. Although the specific mechanism for the removal and inactivation is not fully understood, this process involving adsorption of virus particles to iron oxide species through electrostatic attraction has been often suggested [10, 14]. The inactivation by

strong attachment force which causes the viruses to undergo lysis or become noninfectious has also been suggested in other studies [10, 11]. It should be noted that, in each study, the concentrations and physical characteristics of the iron tested appear to vary. Studies incorporate iron into batch tests in both dissolved and solid form. Contact times and initial virus concentrations also appear to vary quite significantly. Given all the varying testing conditions, direct comparison of removal efficiency data is difficult to judge. However, one thing can be concluded from all the studies: that zero-valent iron can to varying degrees remove and often inactivate viruses in water through corrosion and formation of complex oxides at the iron surface.

2.7 Thesis Overview

This thesis will describe in detail the specific procedure developed to generate a tailored POU filter medium that incorporates nZVI for the enhanced treatment of drinking water. Characterization techniques will be employed to evaluate the efficiency of the synthesis procedure and the generated product itself. To simulate drinking water contaminated with enteric microorganisms, two bacteriophages MS2 and φ X174 will be used as surrogates and batch tests will be performed to measure removal efficiencies for each bacteriophage. The varying effect of phage removal will also be observed by adjusting the percent of iron by weight coated on the surface of GAC. Removal mechanisms will be suggested to explain the observed experimental

data. Finally, drawing on conclusions from the observed experimental data, the potential application of such a POU filter medium will be explored.

Chapter 3

EXPERIMENTAL SECTION

3.1 Filter Media and Reagents

The POU filter media used in this study was GAC (TOD-NGS; 20x50), purchased from Calgon Carbon Corporation (Pittsburg, PA). The incorporation of this specific, processed type of GAC was chosen due to its common commercial use in POU drinking water treatment systems currently on the market. TOG-NDS 20x50 is specifically designed for POU water treatment applications where impurities are removed with short contact times. It is produced from bituminous coal and activated at high temperatures in a steam atmosphere. The finished virgin product has low ash content due to its higher degree of hardness relative to other coal-based raw materials, reducing the generation of fines and product losses during handling and usage. Its particle size is selected to provide efficient removal of volatile organic compounds (VOCs), taste and odor causing constituents, and various residual disinfectants. Ferric nitrate nonahydrate (Fe(NO₃)₃·9H₂O; Acros Organics) was used as a primary source of Fe(III) for iron loading procedures. All compressed hydrogen and nitrogen gas used during synthesis procedures were purchased from Keen Compressed Gas (Wilmington, DE). Adjustments made to solution pH were performed using prepared solutions of

either sodium hydroxide (NaOH), ammonium hydroxide (NH₄OH) or hydrochloric acid (HCl). All solutions were prepared using de-ionized (DI) water (18 M Ω cm) supplied by a centralized DI water system.

3.2 Preparation of Modified GAC

The first modification made to the GAC media incorporates a common groundwater remediation practice of coating GAC with iron salts followed by chemical and thermal reduction of iron to its zero valent state. Commonly reported procedures for coating iron oxides onto GAC generate coated products with high iron yields (15-40 % wt.), primarily relying on adsorption-only mechanisms under acidic conditions. Initially, ferric salt solutions are very acidic and range in pH from 0.5 to 1.5 prior to the addition of the carbon catalyst. Due to the limitations of Fe(III) adsorption at low pH (\leq 3), high concentrations of ferric salt is required to effectively achieve such high iron loadings (15-40 % wt.), which results in costly spent iron-waste. It should also be noted that for small scale POU drinking water treatment systems such heavy iron loadings are undesirable, due to the likely byproducts attributed by excessive iron leaching as proceeds the oxidation of iron. Therefore, to forestall such concerns, both the target iron loading and coating procedure for GAC were appropriately tailored, considering potential regulatory drinking water criteria as well as production cost efficiency.

3.2.1 Coating GAC

The method for coating GAC involves dissolution of a target mass of ferric nitrate nonahydrate in 50 mL of DI water in a 250 mL Pyrex flask using a homogenizer motor drive (Glas-Col) with a Teflon-coated stir shaft under ambient conditions. Upon complete dissolution, a measured mass of GAC was added to the acidic ferric salt solution. The amounts of ferric salt and GAC were determined based on the desired iron loading, which in this study ranged from 3 to 8 percent iron by GAC weight. The ferric-GAC slurry was stirred continuously, allowing all the suspended iron to transfer onto the GAC surface evenly upon further mixing/processing. Previous studies reported that the degree of impregnation of Fe(III) onto the GAC surface increases with the decreasing net positive charge of the GAC [24]. Therefore, given the acidity of the ferric-GAC mixture, in order to achieve the highest degree of iron loading onto the GAC surface the pH of the continuously stirring mixture was gradually adjusted in a drop-wise manner to above 8.5, using a 5 N NH₄OH solution. The target pH of 8.5 was chosen due its close proximity to the zero point charge of iron itself. The goal is that upon reaching set target pH all iron suspended in the solution will ultimately precipitate onto the surface of GAC and, therefore, avoid any wasting of incorporated iron by improving coating efficiency. However, as discussed later in chapter 4, the efficiency of iron coating will decrease as the target iron loading is increased. After mixing, the flask and contents are then removed from the homogenizer and placed in a 70 °C oven for calcination. During

calcination, the heat treatment process will remove any liquid from the slurry and strengthen the iron-carbon bond, mitigating the dissociation of iron from GAC during reduction treatment. Once dry, the ferric-GAC is sieved to remove any fine particles, and to ensure an even particle size distribution.



Figure 3.1 (Right) Stainless steel kiln reactor. (Left) Compressed gas delivery system and muffle furnace.

3.2.2 Reduction and Passivation

Reduction of Fe(III) on GAC to its zero-valent state was carried out at

high temperatures (<800 °C; [21-23]) under a hydrogen atmosphere. Specifically, a

target reduction temperature range from 475 to 500 °C was used. A stainless steel kiln

reactor (Figure 3.1) used to carry out the reduction was fabricated and configured to fit

inside a modified high temperature muffle furnace (Thermolyne Type 1300). The volumetric capacity of the kiln reactor is 78 cm³. A network of stainless steel tubing (McMaster-Carr, Type 316) with two glass ball flow meters (Key Instruments) and three-way ball valve (Swagelok) was constructed to operate as a gas delivery system, in order to regulate and monitor the gas flow rate through the reactor. Post calcination, a measured mass of dry ferric-GAC media was placed inside the reactor and sealed shut with a stainless steel cover and a series of socket cap screws, in order to maintain a strictly anoxic environment during and following reduction. Inside the muffle furnace, the sealed reactor was connected to the compressed gas delivery line which entered through a rear bore hole. An exhaust line, fed through another rear borehole, connected to the reactor outlet and served to carry away spent gas and coatingbyproducts (vented to a fume hood). During reduction, the reactor temperature was monitored using a digital temperature gauge (Omega, model CN1001TC) fed through the rear borehole. The thermocouple of the temperature gauge was situated/wedged in-between the caps of the screws sealing the cover in order to better measure the kiln reactor temperature. The heating time for reduction could be varied, as appropriate, depending on the target temperature and desired valence state of the iron composite. In order to fully reduce iron to ZVI, a predetermined time of 3 hours was used. During the elapsing 3 hours time period, pure regular grade hydrogen continuously purged the kiln reactor at a flow rate of roughly 400 ccm. Following the completed reduction time, the load to the muffle furnace was removed allowing the temperature to decrease

gradually. Once reaching room temperature, the kiln reactor was then purged with regular grade N_2 to minimize Fe(0) oxidation upon exposure to ambient lab conditions. Relying on the trace oxygen concentration present in regular grade N_2 , this controlled premature exposure resulted in the formation of a thin nanometer passivation layer consisting predominantly of magnetite around the zero-valent core. The purpose for using this passivation technique is to mitigate the pyrophoric reaction associated with ZVI's rapid-oxidation which occurs upon immediate exposure to ambient conditions. Given the thermodynamic-instability of ZVI under ambient lab conditions, omitting this passivation step ultimately leads to the exothermic reaction that occurs when the electron-rich ZVI core interacts with the electron acceptor oxygen present in the air. This passivation technique was incorporated into the synthesis procedure following the assumption that rapid-oxidation consumes more electrons than passive-oxidation. After reduction, the nZVI-GAC media is stored under anaerobic conditions for later characterization and performance evaluation.

3.3 Virus Selection and Assay

E. coli bacteriophages MS2 and φ X174 were selected for this study as surrogates for human enteric viruses. MS2 is an icosahedral single-stranded RNA phage with a diameter of 26 nm and an isoelectric point of 3.9 [9]. MS2 was obtained from the American Type Culture Collection (ATCC 15597B1) and grown on bacterial lawns of *E. coli* (ATCC 15597). φ X174 is a somatic, single-stranded DNA phage
with an isoelectric point of 6.6, ranging in diameter from 25 to 27 nm [9]. It was grown on its specific E. coli host (ATCC 13706). Concentrations of active phage were measured by plaque-forming-unit (PFU) assay using the double-layer agar method. The bottom-layer agar medium was prepared on a per-liter basis, using 40 g trypticase soy agar (TSA; Becton, Dickinson and Co.) and appropriately dispensed in 6 mL aliquots into polystyrene culture plates (Fisher). The liter of top-layer agar medium prepared for phage-to-host infection was prepared using 30 g trypticase soy broth (TSB) and 10 g granulated agar (Difco). For phage-to-host infection, 0.5 mL of diluted virus sample and 1 mL of host culture (grown in 3% TSB medium) were individually added to warmed top-layer agar tubes. The tubes were then briefly mixed using a vortex mixer (Dade) before being poured over prepared top-layer agar plates. Following agar solidification, plates were placed top-down in an Isotemp Incubator (Fisher) at 37 °C for 12 and 5 hours, respectively. Following incubation, viable phage concentrations were measured by counting the plaques visible in the bacterial lawn. Concentrations of virus stock solutions were reported in PFU/mL and only plates with 300>PFU>10 were counted.

3.4 Batch Experiment

For each media and phage, three sets of batch experiments were run using different conditions: blank; virgin-media; and nZVi-media. DI water used to prepare buffers was first sterilized at 121 °C for 20 minutes using a Yamato SN300 sterilizer

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to address any potential preexisting-microbial contamination. After sterilization, the DI water was purged with N_2 for several hours to minimize concentrations of dissolved oxygen present in solution. Following the addition of an appropriately measured mass of sodium bicarbonate to prepare the buffer, pH was adjusted to 7.0 \pm 0.05 using prepared hydroxide and HCL solutions. Prior to testing, both virgin and nZVI coated GAC were pretreated with 5 mM bicarbonate buffer under anaerobic conditions. The buffer pretreatment process was of particular importance in the case of GAC media due to its innate alkalinity. Impact of ionic strength on initial virus concentrations was measured using the double-layer agar method in order to address potential concerns with using different ionic strengths. It was concluded that, over the course of 24 hours, no observable change in virus concentration occurred, which is significantly longer than the experimental procedure time.

In order to maintain identical virus concentrations between batch tests, initially 2 liters of virus-buffered solution were prepared for each media and phage. Highly concentrated stock solutions of MS2 and ϕ X174 were diluted in mediaappropriate buffer solutions to reach desired experimental concentrations (10⁴ pfu/mL). Experiments were performed using sterilized 250 mL amber borosilicate bottles. Following addition of 1 gram of either evaluated media, the bottles were filled completely (free of headspace) with virus-buffered solution and sealed immediately with an open-hole screw cap and a Teflon-lined silicone septum (Alltech). The sealed bottles were then hand-shaken end-over-end under ambient lab conditions, ensuring

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that particle terminal velocity was reached for each media. Samples were taken at varying elapsed-time intervals for each batch set in order to develop a plot displaying the kinetic removal. During sampling, 1 mL of virus-free buffer was injected into the bottle through an inserted 1 in. stainless steel side port needle while simultaneously a 1 mL sample was displaced through an inserted 5.5 in. stainless steel side port needle (Alltech). The different needle lengths were used to ensure spatial separation between injection and sampling points in order to prevent virus-sample dilution. The strict use of side port needles was to minimize damage to the septa. Dilutions were made immediately to the samples to avoid possible aqueous-phase inactivation. Viable virus concentrations were then determined by the plaque assay.

Chapter 4

RESULTS AND DISCUSSION

4.1 Nanoparticle Synthesis and Characterization

GAC was coated with ferric salts either by adsorption or precipitation of iron oxides. Synthesis of nZVI was achieved using thermal-hydrogen reduction. Following reduction procedures, the formation of iron nanoparticles was observed on the GAC media. Physical characterization of the nZVI media was determined by total iron analysis, surface area (i.e. Brunauer, Emmett, and Teller (BET) surface area, scanning electron microscope imagery (SEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD).

4.1.1 Iron Quantification via Nitric Acid Extraction

For this study, strong emphasis was placed on developing a procedure for controlling the iron loading on the surface of the GAC. Simply relying on adsorption of Fe(III) onto the surface of GAC during the coating procedure resulted in incomplete loadings and wasted/spent iron. In order to maximize efficiency, the previously described impregnation procedure was employed in order to have full control over iron loading. Total iron measurements were determined for selected batches of GAC, varying in percent iron weight, in order to determine total iron mass on the media and the iron transfer/coating efficiency. This was accomplished through nitric acid extraction followed by iron quantification using ultraviolet and visible (UV-Vis) absorption spectroscopy. Results for an nZVI-GAC sample with a target iron loading of 3%, which was used in the following performance evaluation, are described below as an example.

Table 4.1ABS readings measured using spectrophotometer. Standards are
3% iron by volume and measure comparably to the 3% iron loaded
nZVI-GAC, confirming iron loading control.

Sample	Dilution	ABS Reading
Standard #1	104	0.127
nZVI-GAC #1	104	0.126
Standard #2	104	0.129
nZVI-GAC #2	104	0.128

Initially, a standard iron solution was prepared by dissolving 0.4327 g of ferric nitrate nonahydrate in 100 mL of DI water, resulting in a 10.7 mM ferric nitrate solution with an iron concentration of 600 mg/L. Next, 2 g of nZVI-GAC was added to 10 mL of nitric acid (Fisher, ACS Plus) and mixed in a 50 mL volumetric flask using a Teflon-coated stir bar for 20 min. After mixing, the solution was transferred to a 250 mL flask containing 80 mL of DI water. An additional 10 mL of nitric acid was

added to the acid-washed nZVI-GAC and the procedure repeated. The 100 mL of solution containing acid rinsates and the standard iron solution were then analyzed and compared abreast. Total iron measurements were carried out in 5 mL samples using the FerroVer reagent (Hach) and a UV-Vis spectrophotometer (Hach, DR 5000). Dilutions were made to all samples measured, and duplicates of each sample were also measured for reproducibility. As shown in Table 4.1 the close agreement between the iron extracted sample and standard indicates the nZVI-GAC synthesis procedure described previously could generate nZVI-GAC with a 3% target iron loading. The result illustrates not only the control of nZVI loading at low iron loadings but also that transfer of iron onto GAC was efficient and complete, and that negligible iron loss occurred post calcination during either sieving or reduction.

4.1.2 Brunauer, Emmett, and Teller (BET) Surface Area

BET surface area analysis using a Quantachrome NOVA 2000 high speed gas analyzer was employed to generate nitrogen adsorption and desorption isotherms for the unmodified and nZVI-GAC in order to evaluate the extent of loss in GAC pore/surface area due to iron addition and synthesis procedure. For GAC, its highly porous structure provides numerous sorption sites making it ideal for water treatment applications due to its wider range of contaminant removal capabilities. Specifically, the GAC type used in this study (TOD-NGS) is particularly efficient at removal due to its starting material and manner in which it is produced; hence its heavy use in current POU systems. Consequently, due to its narrow pore structure, loading of iron nanoparticles was strictly confined to the GAC surface boundary. For BET analysis, 1.0 g of both unmodified and nZVI GAC were vacuum-degassed at 150 °C overnight, prior to analysis. Using a five-point calibration, the specific surface areas for the unmodified and nZVI-GAC were determined to be 798 m²·g⁻¹ and 792 m²·g⁻¹ respectively. The negligible decrease in surface area indicates that addition of 3% iron to GAC resulted in an insignificant loss of GAC surface area. Hence, it may be presumed that nZVI coating, while providing new/enhanced capacities for contaminant removal, result in negligible loss of sorption capacity of GAC. This is truly a noninvasive amendment.

4.1.3 Scanning Electron Microscopy (SEM)

A scanning electron microscope (SEM, S4700, Hitachi High Technologies America, Inc.) was used to obtain the surface morphology of the virgin-GAC and nZVI-GAC. Figure 4.1 shows the surface of GAC and its random amorphous surface structure consisting of a broad range of pore sizes and micron scale cracks and fissures. Figures 4.3 and 4.4 illustrate the surface morphology of the nZVI-GAC. Comparing the surface of nZVI-GAC to that of the virgin GAC shows a clear contrast in morphology given the presence of spherical and aggregate particles. More closely examining the zoomed in surface coverage in Figure 4.4, it is very apparent that there is often a high concentration of nanoscale iron particles on the surface which tend to be relatively evenly/densely distributed across the outer surface layer of GAC. The nZVI-GAC surface coverage of spherical particles ranges from 5-50 nm in size and is accompanied by iron aggregates ranging as high as 300 nm. These nanoparticles and aggregates are clearly absent on the virgin-GAC and are presumed to be nZVI particles formed through reduction of coated iron. The variable particle size distribution is suitable for this study given that the entire size range for both spherical and iron aggregates remains in the nanoscale. This confirms that the performed synthesis effectively generates targeted nZVI-GAC.

4.1.4 Energy-Dispersive X-ray Spectroscopy (EDS)

EDS was performed alongside SEM using the images taken for both virgin and nZVI GAC to confirm the presence of iron on the surface along with the general elemental makeup. EDS analysis for both media was performed in which X-rays were detected from the sample excited by a focused, high-energy primary electron beam penetrating into the sample. Figures 4.2, 4.5 and 4.6 show the locations on the surface of GAC for which EDS analysis was performed for either the virgin-GAC or nZVI-GAC samples. Different spectrums were observed for different locations on the GAC surface in order to evaluate the degree of elemental composition. In Table 4.2, the EDS spectrums for virgin-GAC show an elemental composition consisting of primarily carbon in addition to low concentrations of molecular oxygen and sulfur. In Table 4.3 and 4.4, the spectrums for nZVI-GAC show that accompanying the virginGAC elemental structure are observable concentrations of iron. It should be noted, there were several spectrums taken for the nZVI-GAC media targeting different locations. According to the EDS outputs, the surface coverage appeared to vary in the concentration of iron. This suggests that the density of iron coverage observed simply from the SEM images was not as extreme as first believed. Due to the fact that the external surface area of GAC is so vast as well as a lack of extensive EDS data, the exact percent coverage of iron cannot be accurately determined. Despite the percent coverage uncertainty, this analysis still confirms that the synthesis procedure was effective at precipitating iron onto the GAC surface. EDS also showed that the coated iron held its iron-carbon bond throughout the reduction process and sieving procedures. Although this data confirms that the spherical and aggregate particles observed were in fact iron, the valence of the surface iron cannot be ascertained simply using EDS analysis.

4.1.5 X-ray Diffraction (XRD)

To confirm the elemental state of iron on synthesized nZVI-GAC, XRD analysis was performed on a Rigaku X-ray Diffractometer (Ultima IV), using Cu K α radiation ($\lambda = 1.5406$) at 40 kV and a sampling width of 0.02° 2° at a scan speed of 1.0 deg/min. Figure 4.7 displays XRD patterns for nZVI-GAC samples prepared for two different iron loadings (3% and 15%) over a scan range of 20–90°. Identified on both XRD patterns are the three intensity peaks characteristic of elemental iron: 44°, 65°,

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and 82°. These XRD results confirm the presence of ZVI on the surface of GAC and that the nZVI-GAC synthesis procedure successfully reduced ferric iron to its zero-valent state. In addition to the three ZVI intensity peaks identified on the pattern plots, several peaks are also visible in the scan range of 20 to 40°. These peaks are attributed to the crystalline structure of GAC. The most visible is the carbon allotrope graphite whose intensity is highest at 26.6°. In addition to the background peaks from GAC, roughly around 35° a minor peak is visible that resembles the iron oxides, possibly wüstite (FeO) or magnetite (Fe₃O₄), which is indicative of the protective oxide shell casting the ZVI core formed during the post-synthesis nitrogen passivation.

4.2 Batch Experiment

Figure 4.8 and 4.9 displays the removal of MS2 and φ X174 from solution in the 250 mL batch reactors containing 1.0 g of media. The aqueous concentrations of viable MS2 and φ X174 decreased continuously during their respective experimental time periods, during which they appear to follow first-order kinetics. In contrast, in the absence of any media no removal of either virus was observed during the same time periods as shown. Because removal of viruses from water in a batch reactor involves multiple steps, observed first order rate constants may reflect the rate of any one of these processes or their combination: mass transfer of virus from bulk solution to the exterior surface of the filter media; diffusion of virus in pores within the filter media; and adsorption of virus to a surface site [9]. In addition, given that virgin GAC possesses an affinity towards the negatively charged virus particles, the degree of enhanced removal associated with the incorporation of nZVI should reflect the difference between the observed removal rates for both media. Consequently, this potentially restricts focusing heavily on mass transfer as the primary mechanism for virus removal due to the discrepancies between the initial calculated mass transfer coefficient (k_{MT}) for GAC, and the observed rates for the virgin and nZVI coated GAC.

$$\ln[virus] = \ln[virus]_0 - kt \tag{4.1}$$

Using eq. 4.1, the first-order rate coefficients for MS2 removal by virgin-GAC and nZVI-GAC were determined to be 0.037 and 0.0961 PFU·min⁻¹, respectively. The removal rates for MS2 can be observed in Figure 4.8. The first-order rate coefficients for φ X174 removal by virgin-GAC and nZVI-GAC were 0.0298 and 0.0413 PFU·min⁻¹, respectively. The removal rates for φ X174 can be observed in Figure 4.9.

In order to distinguish the contribution of virus removal by mass transfer mechanisms, estimates of the external mass transfer rate coefficient (k_{MT} min⁻¹) were made for each GAC media. When comparing observed removal rates of both virgin-GAC and nZVI-GAC to the mass transfer coefficient, due to the complexity of the system it is difficult to argue that physical mass transfer is the single driving force behind virus removal for nZVI. It should also be noted that the estimated k_{MT} 's for GAC applies to both media conditions. In that regard, it should be clear that one k_{MT}

coefficient really shouldn't be applied to both media given that the parameters used to estimate k_{MT} do not address any chemical reactions that might occur between reacting species and the surface conditions. Therefore, the best application of the estimated k_{MT} is for modeling the removal performance of virgin-GAC. However, the following discussion postulates k_{MT} 's application for attempting to understand the discrepancies in removal rates between the two GAC media (Δ GAC) for each bacteriophage.

4.3 Diffusion-Controlled Mass Transfer

In calculating the mass transfer coefficient for virgin-GAC several assumptions were made. Assuming GAC as a uniform sphere, rates were determined for the physical situation of forced convention around a solid sphere. Initial solute-solvent diffusion coefficients were determined using the Stokes-Einstein equation (eq. 4.2). Using eq.4.2, the diffusion coefficient for the bacteriophages was found to be 1.67E-7 cm²·s⁻¹ at 20 °C. Minimal mass transfer coefficients (k_{\pm}^* ; m·s⁻¹) for both viruses were determined following the approach in Arnold et al. [32]. Due to similarity between the viruses diameter, an average k_{\pm}^* of 2.97E-6 m·s⁻¹ was used for both MS2 and φ X174. It was also suggested that for systems where there is no impeller and mixing is simply done by circulating the fluid the minimal mass transfer coefficient (k_{\pm}) is likely to be 1.2 to 1.5 times greater [33]. The use of 1.5 as a correction factor for k_{\pm} in previous studies showed good agreement with observed experimental data [9, 32]. Therefore, the factor of 1.5 was also chosen for this study

leading to a k_{L} of 4.46E-6 m·s⁻¹. Finally, using the batch-volume of 250 mL and assuming spherical particle geometry, the geometric surface area-to-solution volume ratio (a) for GAC was calculated as 32.2 m^{-1} [34]. Finally, the corresponding external mass transfer rate constant for GAC could be determined as 8.62E-3 min⁻¹($k_{MT} = \alpha \cdot k_L$). Compared to the observed first-order removal rates for virgin-GAC, this k_{MT} value is a clear underestimate. To address this discrepancy and correct for the assumptions made using eq. 4.2, it was necessary to examine the parameters involved in the diffusion and mass transfer calculations. Also, due to the physical conditions of GAC and the complex nature of our batch-system, this type of diffusion-controlled reaction would be representative of a reactive porous catalyst [35]. The reactive nature of our media in fact was never clearly addressed in our calculations due to uncertainties involved in biocolloidal reaction mechanics. Hopefully, by investigating the approaches used by previous studies, we can find a better fit in regards to incorporating the unspecified molecular activities occurring in the system that have previously been disregarded. Simply put, we need to increase the speed of the diffusing virus species to achieve a comparable k_{MT}.

A diffusion-controlled process always involves required sequential steps. In the 250 mL batch-reactor, reactions between the protonated GAC surface and ionic virus particles suspended in solution first requires these species' diffusion together before the reaction takes place. Reactions like these are said to be diffusion-controlled when the diffusion steps take much longer than the reactions steps [35]. In regards to the dispersed iron nanoparticles impregnated on GAC's surface, this reaction can be termed heterogeneous. Specifically, the virus diffuses to the irons surface, the virus quickly reacts with iron, and the virus is either adsorbed or inactivated. The overall rate is determined by the diffusion steps weighted by the equilibrium constant of the surface reaction. In order to estimate this behavior, the particle-boundary interaction can be considered surface diffusion. This term is often used as an excuse for many unexpected observations [36]. Applied to this study, the theoretical assumption for the removal of viruses by virgin-GAC is that diffusion should be a measure of several processes occurring in parallel.

For GAC, the first interaction between the virus (solute) species and GAC occurs at the surface boundary, where diffusion can occur fastest. Taking into account the initial spherical assumption, this would suggest that such a physical condition would produce a rate that overestimates the removal performance due to the loss of slow diffusion in the pores. However, given the combination of GACs charged protonated structure and its affinity towards electronegative virus molecules, porous-diffusion-inhibition can be neglected. This proposed idea can be supported by the dissimilarity between the observed batch removal rates and the calculated k_{MT} for forced convection around a sphere. Therefore, presuming more than one means of diffusion in such complex systems, further diffusive mechanisms were examined. Following diffusion at the surface boundary, a second possible process occurs within the GAC pores. For solute-boundary interactions, as solutes diffuse through the small

pores the alacrity is affected by the size and shape of the pores [35]. In addition to superficial diffusion of particles "through" pores, interactions should also be considered for solute-surface interaction between viruses "trapped" within the pore space or between the pore walls. Collectively, this discussion of diffusion-controlled mass transfer is presented to simply present the possible random molecular motions occurring among the diffusing virus species in aqueous solution, and their diffusion from aqueous phase to the porous media. Consequently, taking into consideration the parameters involved for calculating the viral k_{MT} , diffusion only corresponds to the measure of virus movement in aqueous solution and omits the electrostatic forces between the antipodal charged molecules.

$$D = \frac{k_b \tau}{6\pi\mu r} \tag{4.2}$$

As previously mentioned, the Stokes-Einstein equation was used to estimate the diffusion coefficient used in the mass transfer calculations. In eq. 4.2, parameter k_b is Boltzmann's constant, μ is the dynamic viscosity of the solvent (water), and r is the radius of the solute (virus). The term $6\pi\mu r$ comes from Stoke's law and represents the friction coefficient of slow moving spheres (solute). By interpreting the equation, it would appear solvent viscosity is the driving parameter for estimating diffusion. Assuming viscous drag as the driving factor (therefore proportional to solute speed) obviates the need to analyze the molecular properties of the interacting species. Therefore, diffusion coefficients estimated for this study are all independent of the charge of the diffusing virus species and, therefore, treated as neutral molecules.

4.3.1 Simulating the Actual Situation in a Complex System

Continuing, with the assumption that the virus removal by GAC can be identified as mass transfer-controlled (in which behavior models can be applicable), previously developed adaptations of the Stokes-Einstein equation were employed to find k_{MT} estimates that better fit the removal behavior commonly observed experimentally. Given that solute-solvent molecular interactions are not represented in eq. 4.2, the factor 6π was replaced by a factor of 4π . The substitution of 4π can be rationalized on mechanical grounds [37]. Given the pretermission of molecular species interference, this substitution translates to the solvent slipping past the surface of the solute molecule due to a relatively low solute-to-solvent size ratio [37]. Basically, from observed analysis of virus removal by virgin-GAC it is clear that a significant underestimate was made when calculating mass transfer coefficients as a result of low diffusion estimates. Although the traditional estimates for diffusion appear inchoate for complex systems (regarding discrepancies between predicted and observed removal rates from previous studies), it would appear that the conditions of this study favor diffusion-controlled mass transfer. That is to say, that the measured observed removal rates for virgin-GAC should not be treated simply as the molecular motion of viruses colliding with solvent (water) molecules, after which they reach an impasse as they collide and adsorb at the surface boundary of GAC.

The intention of this discussion is not to suggest that given the known complexity of the batch system in this study, in which the activity between the two reacting species (i.e., virus & media) is independent of mass transfer, that diffusion should be a treated as the sum of all possible diffusion parameters. In order to compensate for the neglected activity, the coefficient used to describe virus diffusion needs to be improved to incorporate the complex reactions between species with shared affinity. This was best achieved by increasing the rate of diffusion, with the assumption that virus mobility is increased in solutions where reactive catalysts are present. Making this assumption also suggests that solute-to-solvent size ratio (within reason) has lesser affect when a solute-ion "sees" an opportunity to react with a highly "attractive" neighboring molecule (GAC). In addition, this improved diffusion coefficient pertains more so to the solute itself and partially dilutes the solute-solvent complex associated with the traditional Stokes-Einstein equation. Despite the mild infringement made to eq. 4.2, it should be noted that the assumptions made to derive the Stokes-Einstein equation can also be argued as mildly presumptuous, especially in view of the experimentally observed viscosity dependence. Nonetheless, using the adjusted eq. 4.2, the diffusion coefficient increased to 2.44E-7 cm²·s⁻¹. Compared to the initial diffusion estimate, we see that the corrected estimate remained in the same order but did increase, roughly, by a factor of two. Proceeding with this improved rate of diffusion, the corresponding k_{MT} is then 1.13E-2 min⁻¹. Compared to the observed rates the improved diffusion coefficient found using the Sutherland equation [37] in turn, generated a k_{MT} comparable to observed reaction rates.

In addition to the factor of 4^{π} substitution, Glasstone [38] proposed yet another substitution of using a factor of 2 instead. This was supported by the theory of absolute reaction rates. In that regard, diffusion is used to represent a rate process occurring in a system. Substituting a factor of 2 in eq. 4.2, we find a diffusion coefficient of 1.54E-6 cm²·s⁻¹, resulting in a k_{MT} value of 3.97E-2 min⁻¹ for 1 g of virgin-GAC. Compared to the observed removal rate for GAC, this estimated rate would definitely defend the assumption of virus removal by diffusion-controlled mass transfer. However, adjusting to a factor of 2 may be too much a stretch by oversimplifying solute-solvent interactions with respect to the presence of a reactive media.

$$D = 7.4 \ x \ 10^{-g} \frac{(xM)^{0.2}T}{\mu V^{0.4}} \tag{4.3}$$

The final diffusion-controlled k_{MT} estimate for our system corresponds to the diffusion coefficient for MS2 (only), determined using eq. 4.3. First proposed in Wilke and Chang et al., eq. 4.3 represents an attempt to generalize the relation of diffusion for unidirectional mass transfer to properties of dilute solutions so as to permit estimation of diffusion coefficients for engineering purposes [39]. Previous studies [9, 32] also mention using this approach when deriving diffusion coefficients for comparing mass transfer to observed removal rate. In eq. 4.3, parameter M is the molar mass of the solvent, V is the molar volume of the solute, and x is an association parameter to define the effective molecular weight of the solvent with respect to the diffusion process (x = 2.6 for water). Based on widely accepted experimental sedimentation data, MS2 is reported to have a molar mass of $3.6E+6 \text{ g}\cdot\text{mol}^{-1}$ and a measured particle density of $1.38 \text{ g}\cdot\text{cm}^{-3}$ [39-41]. Knowing the molecular properties for both MS2 and the batch-solvent, using eq. 4.3, the diffusion coefficient was found to be $2.09E-6 \text{ cm}^2 \cdot \text{s}^{-1}$, corresponding to a k_{MT} of $4.9E-2 \text{ min}^{-1}$. Compared to the "control" removal rate of virgin-GAC, following this empirical approach leads to a k_{MT} that exceeds the observed. Therefore, since the observed first-order removal rate *k* must be smaller than or equal to k_{MT} , using this approach suggests mass transfer as an estimate for modeling virus removal.

However, this k_{MT} only holds true for the lower zero-point-charged virus, MS2. In observing the first order removal rates presented in Figures 4.8 and 4.9, it is clear that the rates for the virgin-GAC and nZVI-GAC do not behave the same for the separate bacteriophages used in the batch tests. To argue that mass transfer can be used to model or predict removal needs to, at the very least, hold true for virgin-GAC and the different bacteriophages. Clearly, this does not hold true. The simple explanation for the discrepancy is likely due to the fact that the physical and chemical (physicochemical) properties of the two bacteriophages are quite different from one another. It does appear, however, that the observed removal rate of φ X174 by nZVI-GAC seems to behave similar to that of virgin-GAC. In this case, it can be concluded that the added advantage of ZVI does not behave as a universal improvement when added to GAC. This also means that a single mass transfer coefficient based on iron percent weight cannot be used to model nZVI-GAC removal of viruses in water given that removal is very much so reacting-species dependent.

The fundamental argument for the use of an adapted Stokes-Einstein equation in complex systems is that diffusion is just that, complex. Diffusion involves many chemical and physical interactions and variances, and although kinetic theories are available to address possible molecular behavior, they often appear to be overly complex. Although only focusing on simple models for diffusion, like that of a solute sphere in a solvent continuum or a virus particle in drinking water, predicted diffusive behavior is unlikely the best method for simulating the actual situation in a complex system.

4.4 Conclusions from Long Term Batch Data Using Different Iron Loadings

After manipulating the methods used to calculate diffusion-controlled mass transfer rates, it was concluded that mass transfer is probably not the most accurate or useful method for predicting or explaining removal behavior. The most important justification for this is that not a single mass transfer rate calculated specifically addressed the presence of iron the surface of GAC. However, mass transfer cannot be completely overlooked. It has relevance in analysis seeking an explanation for the similarities among observed removal trends for nZVI-GAC that vary in percent iron loadings. In Figure 4.10, three MS2 removal trends over a 30-minute time period are presented, corresponding to nZVI-GAC batches prepared using three different percent iron loadings: 3, 6, and 8 percent. Given the fact that removal of φ X174 over a twenty minute period (see Figure 4.9) did not seem to differ greatly from virgin-GAC, long term (30 minutes), removal trends were only observed for MS2. Prior to the long term batch tests, the assumption was that an increase in percent iron loading would be proportional to an increase in removal of MS2. After a series of batch tests using different iron loadings, it appeared that removal was not directly proportional to percent iron loading. The question is, why does there appear to be no significant change when using different concentrations of ZVI?

In previous studies changing the form of iron (or in effect the concentration) appeared to have a significant effect on the degree of virus removal. The important fact to consider when understanding this discrepancy in the lack of improved removal using higher iron concentrations is that this study focused specifically on iron nanoparticles at relatively low concentrations. Given that the surface area of ZVI nanoparticles greatly exceeds the surface area of micron or millimeter sized ZVI particles on a weight basis, when exposed to conditions that favor oxidation of metallic iron, the rate at which nZVI oxidizes is much greater than the rate at which larger ZVI particles oxidize. This is idea is consistent with previous observations that although the high surface area of nZVI may allow for more efficient generation of oxidants, a decrease in reactivity associated with the build-up of iron

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oxides on the surface eventually slows the reaction [43,44]. However, as described in the experimental section, the batch tests were performed under an anaerobic condition (i.e., nitrogen purged buffer solution) which signifies the absence of dissolved oxygen. Now, it is well known that anaerobic oxidation of ferrous iron can occur when in the presence of chemoautotrophic and phototrophic microorganisms which can both obtain their energy by the oxidation of electron donors (iron) however this is not the case with our batch system given lack of both sufficient time and light source. Still, oxidation likely did occur due the presence of some trace dissolved oxygen possibly introduced after nitrogen purging. If dissolved oxygen was present in the batch systems, the initial oxidation of nZVI by O_2 could proceed as a 2-electron transfer process, coupled with a 4-electron transfer process ultimately resulting in the formation of Fe(III) (reactions 3-5; [44]). These reactions could occur on the nZVI surface or could involve transfer of electrons through the iron oxide layers [44, 45].

Observing the trends over the 30-minute elapsed period it appears that all primary removal by nZVI-GAC occurred within the first five to ten minutes, after which removal seemed to level off. It should be noted that the extremely thin dimension and disordered nature of the oxide layer surrounding the ZVI core supports the notions that the oxide phase is able to allow electron passage via tunneling effects or defect sites, thereby conserving the reducing characteristics of ZVI [20]. Following that notion, one likely explanation for describing these limited removal trends is that over a short period all the nZVI particles were simply oxidized, leaving either the ZVI

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core too deeply buried under oxide layers to allow for electron transfer or simply oxidizing the core all together. However, this explanation only addresses why the removal only occurs over a short time period. It does not address why removal trends are the same for the three iron loadings over that short time period or why removal levels off after a short time period. To answer the questions concerning the removal trends, we can start by addressing the limitations of mass transfer. In simplified terms, the basic idea of mass transfer is that over a specific time period there are a specific or set number of physical interactions that are allowed to occur between two different species. In this case, the two different species are the viruses and the surface of GAC. As it was previously mentioned, the percent coverage of iron on the outer surface of GAC was never fully confirmed. SEM imagery could only highlight specific sites on the GAC surface, but even from those images it was clear that iron did not fully encapsulate the surface of GAC. The explanation as to why removal seemed to be universal for the three iron loadings is due to a combination of both limitations brought on by mass transfer and the quick rate of nZVI oxidation. In other words, in the time it took for the nZVI particles to oxidize, MS2 particles were only able to interact with the carbon surface a certain number of times and the probability of interaction with ZVI itself was not high given the extremely large surface area of GAC.

To explain why observed removal seemed to simply level off after ten minutes, one can consider the nZVI oxidation as well. It has often been stated throughout this study that GAC has an extensive surface area, allowing it to have a great sorption capacity. However, that doesn't mean that every sorption site will or can be utilized by the charged particles or contaminants present in the water. In other words, although GAC capacity is substantial it is not unlimited. As shown in the SEM figures for nZVI-GAC, although iron is not evenly distributed over the outer surface of GAC it does often appear in the form of very dense aggregate and particle fields. The oxidation of these dense fields might explain the limited removal by nZVI-GAC after ten minutes. The corrosive behavior of iron is essentially determined by the kinetics of the dissolution of the corrosion products [2]. Given the alacrity of the kinetics occurring in the batch system, as observed by the rapid short term removal, it can be suggested that the dissolution of the dense nanoparticle iron fields in some way causes the redistribution of iron to the remaining percentage of active surface sorption sites. Essentially, any dissolution products evolved from iron corrosion are instantly adsorbed or precipitated back to the GAC surface and iron oxides, causing the diminished capacity of GAC to occur in a domino effect. This is consistent with previous observations that the products of nZVI oxidation are formed by oxidative dissociation followed by precipitation [19, 46]. It would be interesting to observe if the surface morphology of nZVI-GAC changes after being used in batch tests. It might shed some light on explaining the lack of removal capacity after such a short interval. Despite the removal limitations observed, clear conclusions can be drawn from the

analysis of the batch data, which are important when designing intended nZVI-GAC engineering applications.



Figure 4.1 SEM images of the surface of virgin GAC. (Top) Image taken at 5 μ m. (Bottom) Image taken at 1 μ m.



- Figure 4.2 SEM images of the surface of virgin GAC used to measure EDS. Three spectrums are taken at different sites of the GAC surface for elemental distribution.
- Table 4.2EDS measurement outputs for three spectrums taken on the surface
of virgin GAC. Measurements conclude elemental composition is
primarily carbon with traces of molecular oxygen.

Spectrum	Carbon	Oxygen	Sulfur	Total
Spectrum 1	99.35		0.65	100
Spectrum 2	99.36		0.64	100
Spectrum 3	92.2	7.8		100
Maximum	99.36	7.8	0.65	
Minimum	92.2	7.8	0.64	



Figure 4.3 SEM images of the surface of nZVI-GAC. (Top & Bottom) Images taken at 5 µm.



Figure 4.4 SEM images of the surface of nZVI-GAC. Image zoomed in to 500 nm for closer observation of iron nanoparticles.



- Figure 4.5 SEM images of the surface of nZVI-GAC used to measure EDS. Two spectrums are taken at different sites of the GAC surface for elemental distribution.
- Table 4.3EDS measurement outputs for two spectrums taken on the surface of
nZVI-GAC. Measurements conclude elemental composition is
primarily carbon with relatively high concentrations of iron.
Oxygen concentrations have increased due to oxide groups.

Spectrum	Carbon	Oxygen	Sulfur	Iron	Total
Spectrum 1	72.96	13.15	0.24	13.66	100
Spectrum 2	77.49	11.05		11.46	100
Maximum	77.49	13.15	0.24	13.66	
Minimum	72.96	11.05	0.24	11.46	



- Figure 4.6 SEM images of the surface of nZVI-GAC used to measure EDS. Two spectrums are taken at different sites of the GAC surface for elemental distribution.
- Table 4.4EDS measurement outputs for two spectrums taken for the same
nZVI-GAC sample from Figure 4.5. Measurements show a lesser
concentrations of iron than Figure 4.5.

Spectrum	Carbon	Oxygen	Sulfur	Iron	Total
Spectrum 1	77.8	15.52		6.68	100
Spectrum 2	77.09	13.63	0.28	9	100
Maximum	77.8	15.52	0.28	9	
Minimum	77.09	13.63	0.28	6.68	



Figure 4.7 XRD patterns for nZVI-GAC using two different iron loadings: (Left) 3 percent iron loading on nZVI-GAC; (Right) 15 percent iron loading on nZVI-GAC. The three intensity peaks identified are representative of the zero-valent iron XRD pattern.



Figure 4.8 Semi-log plot of first order removal rates for MS2 over a ten minute sampling period. Three rates correspond to three batch samples: control; virgin GAC; and nZVI-GAC.



Figure 4.9 Semi-log plot of first order removal rates for φX174 over a twenty minute sampling period. Three rates correspond to three batch samples: control; virgin GAC; and nZVI-GAC.



Figure 4.10 Plot of removal trends for MS2 over a thirty minute sampling period. Three samples of nZVI-GAC containing different percent iron by weight coatings.

Chapter 5

CONSLUSIONS FOR POTENTIAL APPLICATION

After observing the compiled batch removal data, the apparent ratelimiting removal of the phages suggest that nZVI-GAC may not be best suited for in situ application in everyday gravity-fed drinking water filter systems, as was initially postulated. However, as the data would suggest, with some specification amendments regarding iron loading and the appropriate media mass to treatable water volume ratio, it might be better suited for a one-time-use application. The intention of using these two physicochemically different bacteriophages was to address the broad range of charged microorganisms. Although removal of ϕ X174 by nZVI-GAC did not show appreciable difference from removal by virgin-GAC, there was still a clear observable difference between the batch data for MS2. In this regard, research suggests that by not incorporating nZVI, under POU conditions using virgin-GAC, the results would be suboptimal for removing MS2. Specifically, consumption of water contaminated with microorganisms of similar physicochemical properties as MS2 would pose greater risk for water-related illness brought on by the inefficient treatment of microbial contamination.
5.1 POU Technologies

Currently, there are many POU products out on the market today that are used by individuals who lack access to clean water. This is a common occurrence for hikers or campers who often find themselves miles away from any source of clean drinking water. In these situations, individuals may find abundant sources of "fresh" surface water in the form of ponds, streams, or rivers. Although the "fresh" water may appear clean (or free of any suspended solids or visible particulates), this in no way signifies that it is safe to drink. There is a greater probability of risk that it is what you cannot see that is the most harmful to human health. In such situations, POU water treatment technologies have great utility. Common POU technologies or practices used in field situations to disinfect or sterilize microbial-contaminated water include: boiling water, chlorine pills or drops, iodine drops, and carbon-based materials. There are advantages and disadvantages for each technology mentioned.

Historically, boiling water has been the most common method for sterilizing water. The advantages of boiling water are that it can be completely effective at killing off all harmful microorganisms given enough time. Also, it is a very simple process; all you need is a heat source and a vessel to hold the water. The disadvantages of boiling water are that it takes time to fully sterilize the water sample and it requires a heat source of some kind, which may not always be available or practical. The second POU technology for field application follows the same practice as municipally treated drinking water, using chlorine and its constituents. For field application, chlorine can be purchased in the form of drops and pills and is a great disinfectant when properly used. A disadvantage associated with the use of chlorine as a disinfectant is that taste and odor issues are a common problem with chlorine treated water. More importantly, a disadvantage of chlorine is that it is not as good at killing some of the tougher microorganisms that appear in environmental systems, such as *Giardia* cysts. In Jarroll (1981), the effect of chlorine on *G. lamblia* cysts was examined [47]. The study concluded that at lower water temperatures (< 15 °C), killing of *Giardia* requires relatively high chlorine concentrations and long contact times (30 to 60 minutes).

The third POU technology used in field applications is iodine, which has a long history of use. With regards to microbial disinfection, iodine has been shown to be more effect than chlorine-based treatments in inactivating microorganisms such as *Giardia* cysts [48]. However, there are several disadvantages of using iodine, especially with long-term exposure. Some people are simply allergic to iodine and therefore cannot use it as a form of water purification. Persons with thyroid problems or on lithium, women over fifty, and pregnant women should first consult their physician prior to using iodine for purification due to adverse health effects [48]. Bad taste is another disadvantage for using iodine. The last POU technology presented for field application is the use of carbon-based materials (i.e., GAC). As discussed in previous sections, GAC is widely used for removing organic and inorganic constituents from water. In Hijian (2010), their experimental results demonstrated that *Giardia* cysts could be significantly removed (1-2 log units) using GAC which they concluded largely attributed to the attachment or adsorption of the organisms onto the charged GAC surface [31]. However, a downside to virgin GAC as demonstrated by this study is its limited removal capacity for viruses with varying physicochemical properties.

5.2 nZVI-GAC POU Application

The injection of nanoscale zero-valent iron for remediation of contaminated groundwater is one of the most prominent examples of the application of nanotechnology for environmental improvement. Given the excellent remedial success of ZVI deployed at contaminated groundwater sites, it can be presumed to have similar remedial potential when applied directly to point source drinking water treatment. The focus of this study was to develop and demonstrate an innovative and cost-effective in situ technology for improving the removal efficiency of a currently used POU drinking water treatment technology, GAC. This enhancement was achieved by incorporating nanoscale zero-valent iron onto surfaces of GAC.

The conclusions drawn from this study present an intriguing potential for applying nZVI-GAC as a POU treatment option. Although this study only addressed

the potential for microbial disinfection, ZVI is widely accepted as a viable option for treating a vast array of organic and inorganic waterborne constituents. Since iron poses no serious health threat to higher organisms, there are no potential concerns associated with incorporating it into current drinking water treatment systems. Taking into consideration any adverse health related concerns as well as aesthetically displeasing side effects such as odor and taste, chemical disinfection by means of chlorine and iodine may not be the best solution for treating contaminated water in the field for personal consumption. Although boiling water is a sure bet for sterilization, it is simply impractical in many field situations. Carbon-based media are widely used, due to their removal efficiency for a variety of contaminants from drinking water, with an added bonus of low production cost. Ultimately, drawing on the conclusions from this study, the engineered application of nZVI-GAC is suggested as a substitute for the conventional in-the-field POU technologies. Using this media, the aesthetically displeasing side effects associated with chemical disinfection can be avoided, while still providing the added benefit of enhanced disinfection or removal due to the nZVI in addition to the removal mechanisms attributed by the carbon media itself.

Although this engineered application shows promise as an improved inthe-field POU technology, further extensive testing needs to be performed to better understand the reaction mechanisms that lead to higher removal efficiency. In addition, the applied method for delivered exposure of the nZVI-GAC media to the contaminants present in the water is an important design factor to consider. It is likely that a simple gravity-fed system may be unsuitable for optimal utilization of the incorporated nZVI. A design that allows nZVI-GAC to be in continuous suspended contact with the drinking water undergoing treatment might be more suitable given that, as previously suggested, it is the combination of electrostatic mechanisms of the ZVI core as well as the resulting oxide species that are considered to be the focus for enhanced removal. Therefore, by allowing the nZVI-GAC to remain in suspension longer, the formation of complex iron oxides can proceed, while at the same time increasing the contact time between the media and the suspended contaminants, ultimately enhancing the overall removal efficiency. This would not occur when using gravity-fed systems, for which contact times are limited. Altogether, further research will be necessary in order to develop the exact synthesis procedure that generates an nZVI-GAC media tailored to satisfy U.S. EPA water quality standards.

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