REMOVAL OF ARSENIC CONTAMINATION FROM WATER USING MAGNETITE NANOPARTICLES

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Introduction:

Water contamination is a global problem that can result in illness and death. Consumption of contaminated drinking water is particularly problematic in third world countries where inadequate purification processes, coupled with rapidly increasing population growth and industrialization pose serious health risks. One of the most common and deadly contaminants found in water is arsenic (As). Arsenic, a heavy metal, is a key toxic contaminant in the drinking water supply of third world countries, often exceeding 10 µg/L maximum limit set by World Health Organization (WHO) regulations (World Health Organization, 2006). As contamination of drinking water is also found domestically, where 13 million people in the United States are affected by exposure; these numbers dramatically increase where drinking water restrictions are less rigid. For example, 45-57 million people in Bangladesh have been exposed to 10 µg/L or more of arsenic in water (Yang, 2010). The necessity of an effective system to remove arsenic from water is all too great. Current methods employed in some countries lack sensitivity, and are only effective in dealing with large concentrations of arsenic in water, such as 100 µg/L. These systems often leave residual As concentrations above the 10 µg/L restriction set by WHO, (Pittman, 2007). System enhancements are possible, but the cost of improvements remains prohibitive for many areas. However, recent studies have demonstrated that iron oxides have a high affinity for heavy metals such as arsenic and have opened the door as a cost-effective way to remove pollutants from water (Yavuz et al. 2009). Ferrofluids, which are suspensions of nanoparticles of magnetite (a ferrous-ferric oxide), are magnetic, stable, colloidal, and homogenous. (Maity, 2006). Such particles are typically suspended in a carrier and can respond to a magnetic field but retain no residual magnetism once the field is lifted. Magnetite nanoparticles in a liquid carrier can be manipulated by a magnetic field, retain no residual magnetic properties, and have demonstrated the general iron oxide affinity for heavy metals (Yavuz et al 2009).

In the current investigation, the adsorption of arsenic by magnetite nanoparticles was evaluated. Additionally, methods and conditions that facilitate the removal of As by nanoparticles was evaluated. Results of optimized conditions were compared to WHO standards and data from previous studies to accurately gauge the accuracy of results and applications thereon. Due to the small particle size, easy manipulation, and cost effectiveness of production, use of magnetite nanoparticles to remove arsenic from water could prove to be very feasible, particularly in less industrialized countries. Altered conditions in this investigation were pH and the surfactant type. Three types of nanoparticles were tested- bare (uncoated), oleic acid coated, and humic acid coated. Different methods regarding nanoparticle generation and coating were attempted before the final particles were generated, and were then coated with oleic acid (Yavuz et al. 2009) and humic acid (Liu et al. 2008) respectively.

Materials and Procedures:

Various methods for the production of ferrofluids were investigated. Ultimately a precipitation method was optimized and used for the generation of the particles (Berger, 1999). Five milliliters of iron (III) chloride were mixed with 1 milliliter of iron (II) chloride in a flask. The solution was stirred through nanoparticle production using a small magnetic stir bar and a magnetic stirrer. Ammonium hydroxide (NH_4OH) (50 ml) was slowly added to the flask in a drop-wise fashion over the course of 5 minutes. The ammonium hydroxide acted as a stabilizer in the synthesis of the iron chlorides. The black magnetic precipitate was removed and placed into a stock flask. Repeated batches of nanoparticles were generated and pooled to insure a uniform stock for subsequent experiments. Prior to coating with surfactants, the nanoparticles were separated into three aliquots, with two of the aliquots used to produce oleic and humic acid coated nanoparticles.

The oleic acid was generated using a modified kitchen method as described by D’Couto, 2008. Reagent grade sodium hydroxide (NaOH) was dissolved in 30 milliliters water, and 100 mL of olive oil was added to the mixture. The mixture was stirred vigorously until a thick, homogeneous liquid (soap) was formed. The soap was left in a ventilated area to dry, cure, and harden. The hardened soap (60 grams) was minced into small chunks and then was mixed with acetic acid (9% acidity). The solution was heated to approximately 100° Celsius, with vigorous stirring for 45 minutes The resulting mixture had two distinct layers; a large syringe was used to remove the top, yellow, organic layer, which was primarily oleic acid (Yavuz et al. 2009).

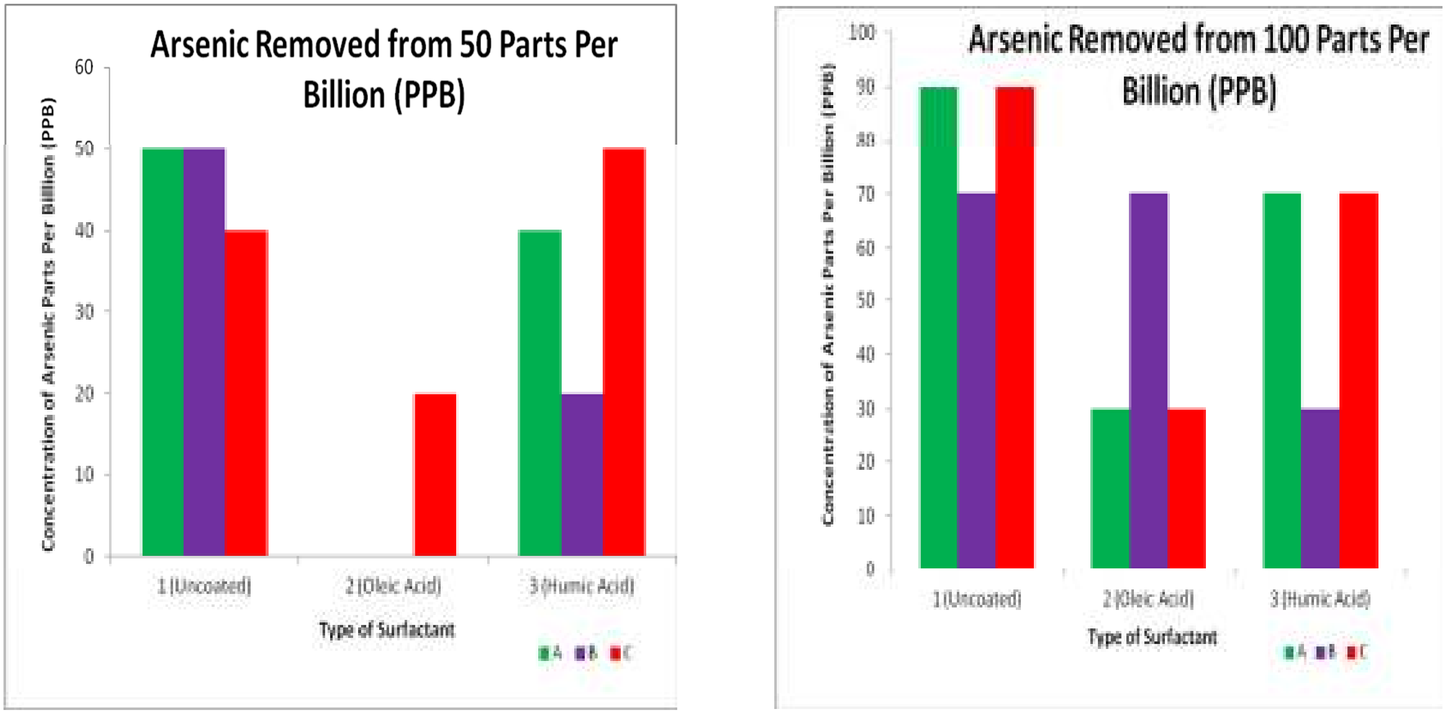
Oleic acid coated nanoparticles were produced in triplicate. Three beakers containing equal concentrations of magnetite nanoparticles were heated to 80°Celsius. Simultaneously, a solution containing 5 milliliters of acetone and 100 µL of oleic acid was prepared. This solution was added to each beaker containing nanoparticles. Additional 200 µL of oleic acid were added to the heated solution at 5 minute intervals to achieve a total of 1 mL of oleic acid in the nanoparticle solution. The beakers remained on the hot plate for 30 minutes at 80° Celsius, before being removed to cool to room temperature. Beakers were then placed on magnets, suspending the particles. The particles were flocculated with acetone, washed with an ethanol-acetone mixture five times (Maity, 2006) and collected using a magnet. Humic acid coated nanoparticles were also generated in triplicate using a method described by (Liu et al 2008). Briefly, humic acid (0.5 grams) was dissolved in 50 milliliters of water. This solution was added to the three beakers (flasks) containing nanoparticles and stirred within flasks for 30 minutes at 90° Celsius. The humic acid coated nanoparticles were removed from each flask using magnetic facilitated decanting.

Adsorption of Arsenic

To quantify nanoparticle concentration, one milliliter of each of the 9 nanoparticle aliquots (three oleic acid coated, humic acid coated and bare nanoparticles) was placed into an incubator overnight to evaporate all liquid. After 24 hours, the samples were removed from the incubator, cooled and weighed. Calculated concentrations were used to ensure an equal number of nanoparticles per test. Stock arsenic solution was prepared by diluting 1 µg/L of the arsenic stock with 1000 mL of distilled water. This stock was used to determine standard of deviation and to perform subsequent tests. The 4 contaminated (test) solutions were 50 ppb (parts per billion of As), 100 ppb, 500 ppb, and 1000 ppb. Using these solutions, 1 mg of nanoparticles were placed in a beaker containing arsenic contaminated solution and allowed to incubate at room temperature for 30 minutes (based on optimal time for As removal in previous studies done at Rice University). The test solution was then removed from the nanoparticles, which was facilitated by magnetic aggregation of the nanoparticles. The test solutions were then used to deter mine As concentration using a colorimetric method (Hach, Low Level Arsenic Test Kit).

Results and Discussions

The results demonstrate that the uncoated, or bare, magnetite nanoparticles were the most effective in the removal of arsenic from the water, when compared to the results of the nanoparticles with the humic acid and oleic acid surfactants. There are several possible explanations that could serve as plausible reasons for the results. First, the generation of the nanoparticles for the current study differed from those reporting that As removal was greater for surfactant-coated nanoparticles. This investigation utilized ammonium hydroxide (NH_4OH) and two different types of iron chloride ($FeCl_2$ and $FeCl_3$), while the studies of surfactant coated nanoparticles utilized only one type of an iron base. Because iron chloride was utilized, the resulting iron oxide base is coated with both ammonium hydroxide and chloride. The exact chemical formula is 2FeCl3 +FeCl2+8NH3+4H2O --> Fe3O4 +8NH4Cl. When adding the ammonium hydroxide to the iron chloride mixture, the solution's color change was palpable, indicating the formation of the ferrofluid as the color transitioned from rusty red to a dark liquid with a black, gelatinous substance at the bottom of the flask. It was found that the slow addition of the ammonium hydroxide proved to be key to the nanoparticle generation. A possible explanation is the contaminant (As). Unlike other types of heavy metals such as lead, arsenic is able to form both mono and bidentate linkages in the presence of iron oxides. Bidentate linkages are a type of ligand binding in which an ion or molecule binds to the



Graphs of Arsenic Removal Tests. Graph 1 indicates the arsenic removed from 50 ppb concentrations. 1,2,3 represent uncoated, oleic acid, and humic acid coated particles respectively. 1-3 signify the type of coating; each one had three trials. A,B,C represent the three trials in 50 ppb concentration of arsenic. Likewise, Graph 2 is organized in a similar manner, except concerning 100 ppb of arsenic.

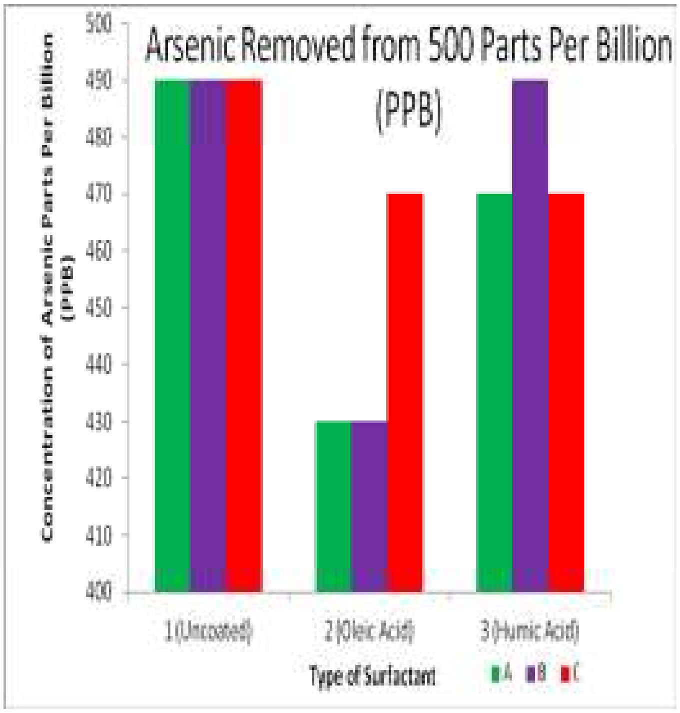
central atom (Fe) to form a coordination complex. In the context of this investigation, bidentate linkages refer to a ligand that binds to two sites; in this case, arsenic. The presence of iron (II) and iron (III), present due to the different types of iron chlorides used in the generation of the nanoparticles in this experiment, leads to the generation of a larger number of potential bonding sites. The increasing prevalence of iron on the nanoparticle could be made inaccessible (i.e., steric hindrance) with the addition of a surfactant (oleic acid or humic acid) to the nanoparticle. It is also common for ligands to be derived from anionic precursors, which include chlorides, increasing the possibility for the arsenic molecules to bond to the iron (II) and iron (III) chloride based oxide sites. While iron chloride was used to synthesize the magnetite, the result is actually iron oxide. The chemical change occurs because of the addition of ammonium hydroxide, creating an iron oxide particle. However, because chloride was a part of the original iron in the reaction, bonding sites on the particle themselves still retain traces of the chloride, creating anionic precursors for ligands.

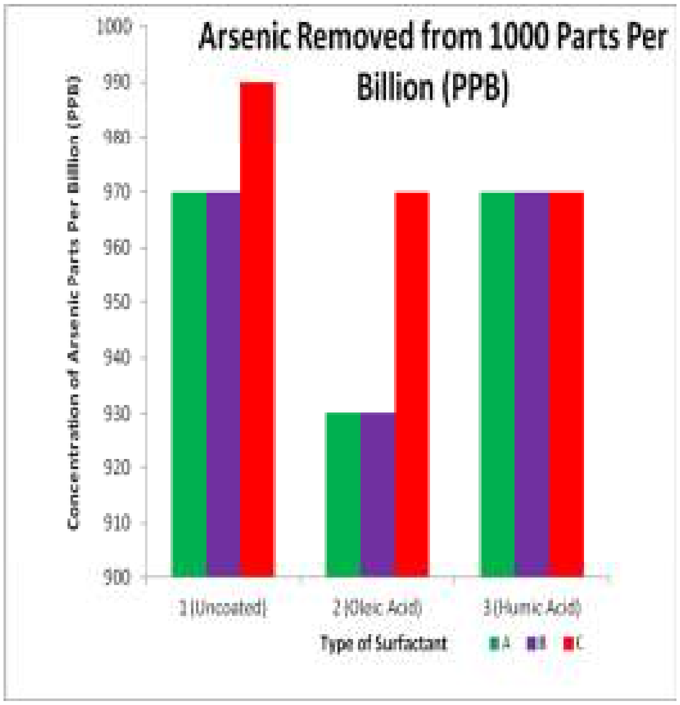
The results did indicate great aptitude for utilizing magnetite nanoparticles in terms of arsenic remediation. Curiously, all of the different types of magnetite nanoparticles performed their best when placed in the 500 ppb and 1000 ppb (or 1 µg/L) solutions of arsenic, remediating well over 90% of the heavy metal. The most effective nanoparticles were uncoated, averaging a removal rate of 93%, with a remarkable 98% removal rate of arsenic in the 500 ppb and 1000 ppb solutions respectively, meeting the stringent United States Environmental Protection Agency (EPA) regulation of 95%, demonstrating the potential applicability of the surfactant free particles for usage in arsenic remediation.

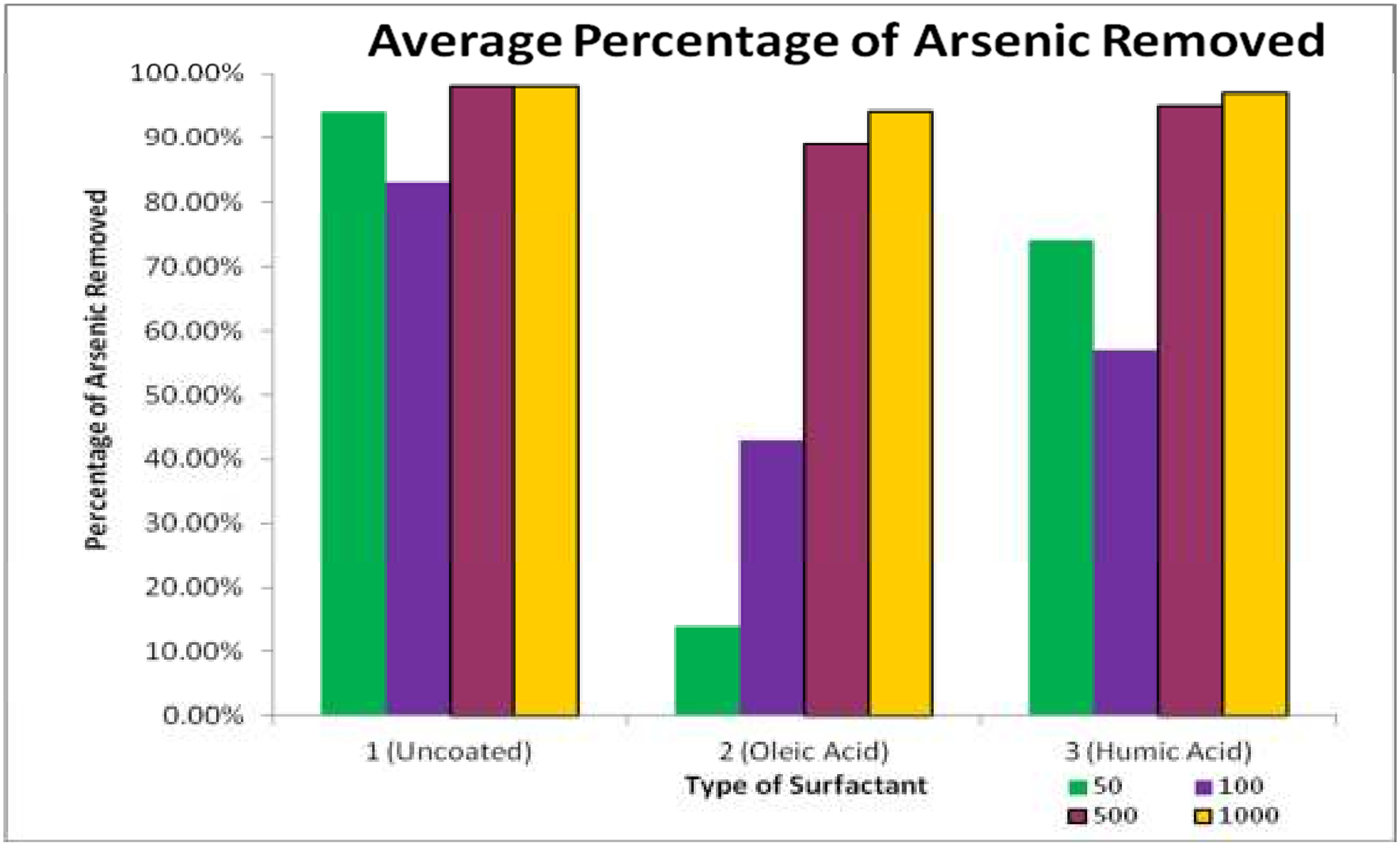
The humic acid particles averaged a removal rate of 81%, with an excellent average removal rate of 95% and 97% for the 500 ppb and the 1000 ppb contaminated solutions respectively. Humic acid itself is an acid based on organic material that is able to form metal ions and bind with metal based atomic complexes. The particles performed best in solutions containing higher concentrations of arsenic contamination, indicating perhaps that the strength of the bond and attraction of the humic acid to both the iron (II) and iron (III) oxides in the magnetite nanoparticle as well as to the arsenic molecules in the self-contaminated solution (Liu 2008).

The oleic acid particles performed the worst out of the tested surfactant types, averaging an arsenic removal rate of 60%. Notably, the oleic acid particles were still able to perform admirably removing 89% and 94% of the arsenic in the 500 ppb and 1000 ppb solutions respectively. However, the main purpose of the oleic acid surfactant was to aid the aggregation of the particles (Maity 2006), as opposed to directly aid with remediation given the current standard that doesn't show any affinity between oleic acid to heavy metals However, the As removal percentage of the oleic acid nanoparticles in the 1000 ppb solutions was just under the mandated EPA parameter, demonstrating that the particles could have the potential to remediate arsenic at higher As levels. It should be noted that removal values were as low as 14% (100 ppb solution) for the oleic acid nanoparticles, and that the standard of deviation and the percentage of error was highest in the tests utilizing the oleic acid surfactant.

A plausible explanation for the greater effectiveness in the uncoated particles but a lower level of efficiency in the particles with surfactants is due to the agglomeration of the particle. Agglomeration refers to how the particle came together. A ferrofluid is a stable colloidal homogeneous suspension of magnetic nanoparticles (Maity, 2006). Several methodologies have been used to generate nanoparticles in previous studies; results may differ based on the technique used for nanoparticle generation. This investigation utilized a combination of iron (II) chloride and iron (III) chloride with ammonium hydroxide, and generated a ferrofluid that was largely homogeneous before the addition of the surfactants. Upon placing a flask containing the ferrofluids on a magnet, the particles would disperse and stand rigid due to the magnetic field, but would fall and clump together once the magnetic field was removed. This demonstrates the super paramagnetic (SPM) property of the particles, indicating that it was a ferrofluid as it exhibited a magnetic attraction but failed to retain residual magnetism following the removal of the field (Maity, 2006). It is to be noted that a different method involving rust as the iron oxide base was attempted (D'Couto, 2008) but the resultant material, while magnetic (Yavuz et al. 2009) was a definite, black, granular substance that lacked the SPM property to define the particle as a colloidal homogenous structure in a carrier liquid. The primary purpose behind a surfactant is to aggregate the particles to help create the ferrofluid and stabilize the nanoparticles. Furthermore, a ferrofluid retains no residual magnetism, and is only able to attract particles based on the affinity for another molecule (through the iron oxides) and the number of available sites for the bonding of particles to the surface of the magnetite nanoparticle. It is possible







This graph compares performance of each type of surfactant (uncoated, oleic, and humic) in each concentration of arsenic (50,100,500,1000 ppb). Each colored bar is the average ppb of arsenic removed for that concentration for a specific surfactant. That means that the first green bar in uncoated (group 1) represents the average arsenic removed by uncoated magnetite nanoparticles in a 50 ppb arsenic solution. From here, the performance of each type of particle can be compared to determine effectiveness.

that the addition of a surfactant may have lowered the number of available sites on the surface of the particles, as well as had an effect on whether the particles were aggregated. Regarding the coating of the humic acid nanoparticles, the primary ingredient of humic acid is there to serve as a polyanionic organic coating on the metal oxide particles, thereby affecting the surface properties of the particles (Liu et al. 2008).(The findings in this investigation are supported by a previous study concerning arsenic (V), lead (II), and cadmium (III) that showed increased arsenic adsorption by particles without a surfactant (D'Couto 2006), but the surfactants tested previously were different from the ones used in this study. However, the current data does demonstrate the feasibility and affinity of uncoated magnetite nanoparticles for the removal of arsenic (and possibly other types of heavy metals and water pollutants), and that magnetite nanoparticles with surfactants do have the potential ability to perform at stipulated standards.

Regardless, the results of this investigation affirm the usage of magnetite nanoparticles to remove arsenic from contaminated water. Arsenic is one of the most malignant pollutants in humanity's most precious commodity, and the size, cost, and efficiency of the processes utilizing ferrofluids to remove heavy metals make it the ideal methodology to combat arsenic contamination. The effects of the nanoparticles themselves in the environment has yet to be explored, and serves as an extension to this investigation. While the surfactant free nanoparticles are demonstrated to be the optimal type of magnetite nanoparticles, investigation into surfactants (the humic acid in particular due to its proven performance, as well as others) could prove to be beneficial. Further extensions include the usage of magnetite nanoparticles for the removal of other heavy metals; while arsenic is the most common and dangerous, the results from this investigation could prove to draw parallels when pitted against similar contaminants. The knowledge gained is a testament to the feasibility and the aptitude of magnetite nanoparticles for the removal of arsenic from water, and can be used to save hundreds of millions of lives from exposure to such a dangerous and hazardous threat.

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Works Cited:

1) Berger, Patricia. "Preparation and Properties of an Aqueous Ferrofluid." Journal of Chemical Educations. 76.7 (1999): 943-948. Print.

2) D'Couto, Helen. "Development of a Low Cost Sustainable Water Filter: A Study of the Removal of Water Pollutants As (V) and Pb (II) Using Magnetite Nanoparticles." Journal of the Us SJWP. (2008): 32-45.

3)"EXPERIMENT 10: PREPARATION AND PROPERTIES OF AN AQUEOUS FERROFLUID." . N.p., n.d. Web. 11 Nov 2011. <http://www.usask.ca/chemistry/courses/231/pdf/Ferrofluid.pdf>.

4) Hach Company, . "Arsenic Test Kit." (2000): n. page. Print.

5) Liu, Jing-Fu, Zong-Shan Zhao, and Gui-Bin Jiang. "Coating $Fe_3 O_4$ Magnetic Nanoparticles with Humic Acid for the High Efficient Removal of Heavy Metals from Water". Environmental Science Technology. Vol. 42, No. 18. (2008): 6949-6954. Print.

6) Maity, D., and Agrawal D.C. "Synthesis of iron oxide nanoparticles under oxidizing environment and their stabilization in aqueous and non-aqueous media." Journal of Magnetism and Magnetic Materials. (2006): 46-55. Print.

7) Nassar, Nashaat. "Rapid removal and recovery of Pb(II) from wastewater by magnetic nanoadsorbents." Journal of Hazardous Materials. 184. (2010): 538-546. Print.

8) Pan, Bingjun, Hui Qiu, Bingcai Pan, Guangze Nie, et al. "Highly efficient removal of heavy metals by polymer-supported nanosized hydrated Fe(III) oxides: Behavior and XPS study." Water Research. 44. (2010): 815-824. Print.

9) Yang, Weichun, Amy T. Kan, Wei Chan, Mason B. Tomson. "pH Dependent Effect on Zinc on the Arsenic Adsorption to Magnetite Nanoparticles". Water Research. Volume 44. (2010): 5693-5701. Print.

10) Yavuz, Cafer, J. Mayo, Carmen Suchecki, Jennifer Wang, Adam Ellsworth, Helen D'Couto, Elizabeth Quevodo, and Arjun Prakash. "Pollution Magnet: Nano-Magnetite for Arsenic Removal from Drinking Water". Environmental Geochemistry Hearth. 2009: Print.

11) Yu, William, Joshua Falkner, Cafer Yavuz, and Vicki Colvin. "Synthesis of monodisperse iron oxide nanocrystals by thermal decomposition of iron carboxylate salts." Royal Society of Chemistry. (2004): 2306-2307. Print.

12) "Water-Related Diseases". Water Sanitation and Health. World Health Organization, 2011. Web, 4 Oct. 2011. <http://www.who.int.water-sanitation_health/diseases/lead/en/>.

13) Mohan, D., & Pittman, C. U. (2007). Arsenic removal from water/wastewater using adsorbents—A critical review. Journal of Hazardous Materials, 142(1–2), 1–53.