

***REMIEDIATING MERCURIC IONS VIA FUNCTIONALIZED MAGNETIC  
NANOPARTICLES***

A Thesis  
Presented to  
The Academic Faculty

by

Austin Landry Bennett

In Partial Fulfillment  
of the Requirements for the Degree  
B.S. Chemistry-Research Option in the  
School of Chemistry & Biochemistry

Georgia Institute of Technology  
December 2013

***REMIEDIATING MERCURIC IONS VIA FUNCTIONALIZED MAGNETIC  
NANOPARTICLES***

Approved by:

Dr. John Zhang, Advisor  
School of Chemistry & Biochemistry  
*Georgia Institute of Technology*

Dr. Kent Barefield  
School of Chemistry & Biochemistry  
*Georgia Institute of Technology*

Dr. William J. Baron  
School of Chemistry & Biochemistry  
*Georgia Institute of Technology*

Date Approved: 13 December 2013

## **ACKNOWLEDGEMENTS**

I wish to thank Dr. John Zhang for his guidance as my principle investigator throughout my research at Georgia Tech. I also wish to thank my fellow Zhang Research Group members for their support over the past two years. I am also indebted to Dr. Yongsheng Chen and Dr. Songyan Du for their willingness to let me use their ICP-MS and their instruction throughout the process. Lastly, I would like to thank Dr. Barefield for his guidance throughout the thesis writing process and the rest of the School of Chemistry & Biochemistry faculty for their instruction both inside and outside of the classroom.

# TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	iii
LIST OF TABLES	v
LIST OF FIGURES	vi
LIST OF SYMBOLS AND ABBREVIATIONS	vii
SUMMARY	ix
<u>CHAPTER</u>	
1 Introduction	1
2 Materials & Methods	4
Nanoparticle Synthesis	4
Coating Methods	5
Remediation & Analysis	5
3 Results	7
Coating Confirmation via XPS	7
Remediation Analysis via ICP-MS	10
4 Future Work	15
REFERENCES	18

## LIST OF TABLES

	Page
Table 1: ICP-MS data showing $\text{Hg}^{2+}$ removal and percent $\text{Hg}^{2+}$ remaining for A.	11
Table 2: Density-dependence data for optimal mass/volume ratio for ligand A.	12
Table 3: Exposure time data determining minimum exposure time for for ligand A.	13
Table 4: Proposed $\text{Hg}^{2+}$ removal experiment with ligands C and D.	15
Table 5: Proposed density-dependence experiment for ligands C and D.	15
Table 6: Proposed exposure time-experiment for ligands C and D.	16

## LIST OF FIGURES

	Page
Figure 1: The structure of the carboxylic acid ligands.	2
Figure 2: The structure of the organosilane ligands and TEOS.	2
Figure 3: Carboxylic acid coating XPS S <sup>2p</sup> spectrum.	7
Figure 4: TEOS coating XPS Si <sup>2p</sup> spectrum.	8
Figure 5: APTES coating XPS N <sup>1s</sup> spectrum.	9
Figure 6: MPTMS coating XPS S <sup>2p</sup> spectrum.	9
Figure 7: Hg <sup>2+</sup> remediation XPS Hg <sup>4f</sup> spectrum.	10
Figure 8: ICP-MS calibration curve for Hg <sup>2+</sup> concentration calculations.	11
Figure 9: Density-dependence experiment results for ligand A.	13
Figure 10: Exposure-time experiment results for ligand A.	14

## LIST OF SYMBOLS AND ABBREVIATIONS

A	3-mercaptopropionic acid
B	lipoic acid
C	aminopropyltriethoxysilane
D	mercaptopropyltrimethoxysilane
EPA	Environmental Protection Agency
MNP	Magnetic Nanoparticles
APTES	aminopropyltriethoxysilane
MPTMS	mercaptopropyltrimethoxysilane
TEOS	tetraethoxysilane
DTT	dithiothreitol
XRD	X-ray Diffraction
XPS	X-ray Photoelectron Spectroscopy
SQUID	Superconducting Quantum Interference Device
ICP-MS	Inductively-Coupled Plasma Mass Spectrometry



## SUMMARY

Mercuric ions,  $\text{Hg}^{2+}$ , display a unique affinity for sulfur-containing biomolecules because of the soft acid/soft base interaction between  $\text{Hg}^{2+}$  and sulfur.<sup>1</sup> Many of these biomolecules are used in signal processing and response;<sup>2</sup> therefore,  $\text{Hg}^{2+}$  is a potent neurotoxin. Chronic exposure to high  $\text{Hg}^{2+}$  levels can lead to mercury-poisoning and even death. This research will focus on removing  $\text{Hg}^{2+}$  from water. Cobalt ferrite nanoparticles will be used to separate  $\text{Hg}^{2+}$  ions from water. A fair amount of research has been conducted using ferromagnetic nanoparticles and various nitrogenous and oxygen-based ligands, such as triazene compounds and tartrate ligands, to remediate mercuric ions.<sup>3,4</sup> Magnetic nanoparticles (MNPs) were coated with thiol-containing carboxylic acid ligands to bind  $\text{Hg}^{2+}$  ions. To combat thiol oxidation, the weak reducing agent dithiothreitol (DTT) will be introduced into the  $\text{Hg}^{2+}$  solutions. The density of the particles in the  $\text{Hg}^{2+}$  solutions and exposure times were varied in order to determine the optimal levels for  $\text{Hg}^{2+}$  removal. In future work, thiol-containing organosilane ligands will be coated onto the particles and tested for  $\text{Hg}^{2+}$  removal to be compared against the carboxylic acid ligands.

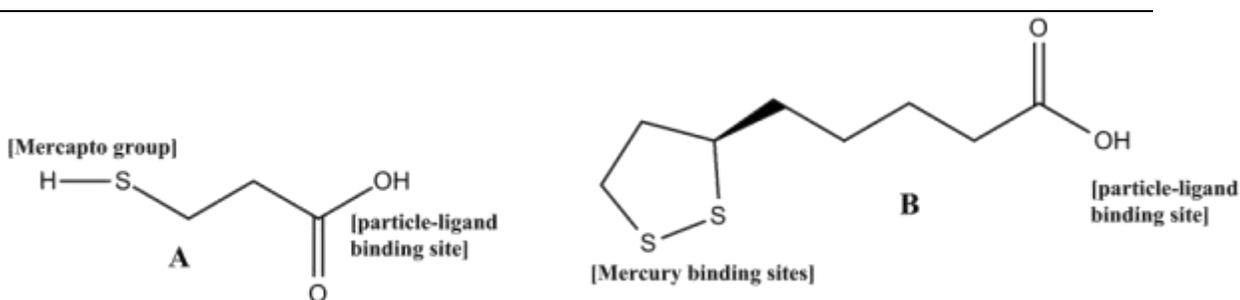
# CHAPTER 1

## INTRODUCTION

Since Drexler's work in the 1980s,<sup>5</sup> nanoparticles have been of interest to researchers from a plethora of disciplines. Magnetic nanoparticles, specifically, have been of interest in environmental initiatives, biomedicine, electronics, etc.<sup>6</sup> Of particular interest to this research are environmental initiatives, more specifically the purification of drinking water using ferromagnetic nanoparticles coated with ligands. Cobalt ferrites are the nanoparticles to be coated with the ligands. Because ferromagnetic nanoparticles are paramagnetic, the particles most easily induced will be the most efficient in ligation and, thus, most suitable for this experiment. The important characteristics of the magnetic nanoparticles are size and hysteresis, perhaps susceptibility. In our previous research, cobalt ferrites have been shown to be 6.87nm in size and have the following magnetic properties:  $M_s = 1.00$  emu/G g,  $M_R = 0.61$  emu/G g, and  $H_C = 9032.41$  Oe. Cobalt ferrites' high coercivity makes them most applicable for the environmental initiatives on which this research is based. Cobalt ferrites exhibit the spinel nanocrystal structure. Spinel-type structures have the generic formula  $MFe_2O_4$ , such that M symbolizes the different divalent metals used in the synthesis. In this case, the metals had a charge of +2 and the iron atoms a charge of +3.<sup>7</sup> Several different methods have been developed for synthesizing magnetic nanoparticles such as microemulsion,<sup>8</sup> solution phase reduction,<sup>9</sup> hydrothermal<sup>1,0</sup>  $\gamma$ -ray radiation-oxidation,<sup>11</sup> biosynthesis,<sup>12</sup> and the aminolytic method.<sup>13</sup> Even trace amounts of mercury can be toxic. The EPA recommended limit for chronic  $Hg^{2+}$  levels in freshwater is 0.77  $\mu\text{g/L}$ .<sup>14</sup> There are, however, several places in the world where  $Hg^{2+}$  levels are much higher, such as China's Northern Yellow Sea (1.1  $\mu\text{g/L}$ ).<sup>15</sup> A fair amount of research has been conducted using ferromagnetic nanoparticles and various ligands, such as triazene compounds and tartrate ligands, to remediate  $Hg^{2+}$ .<sup>16,17</sup>

Roufouei *et. al.*<sup>16</sup> investigated the effectiveness of triazene ligands in separating specifically mercuric ions from water. Our ligands of choice are thiols due to the mercuric ion's strong binding sulfur due to the soft acid/soft base interaction. The strong  $\text{Hg}^{2+}$  binding to sulfur is evidenced by its interaction with sulfur-containing biomolecules.<sup>1</sup> We intend build upon former successes, particularly the success with dithiocarbamate ligands.<sup>18</sup>

It has been shown that carboxylic acid chains strongly adhere to oxide surfaces.<sup>19</sup> Cobalt ferrites,  $\text{CoFe}_2\text{O}_4$ , have an oxide surface. Therefore, a carboxylic acid chain with a mercapto group on the opposite end should bind well to the cobalt ferrites while allowing the mercapto group to hang off the particles. To coat the cobalt ferrites, the method developed by Vestal and Zhang<sup>20</sup> can be modified for the ligands under investigation. The structures for the carboxylic acids to be used are shown in Figure 1.

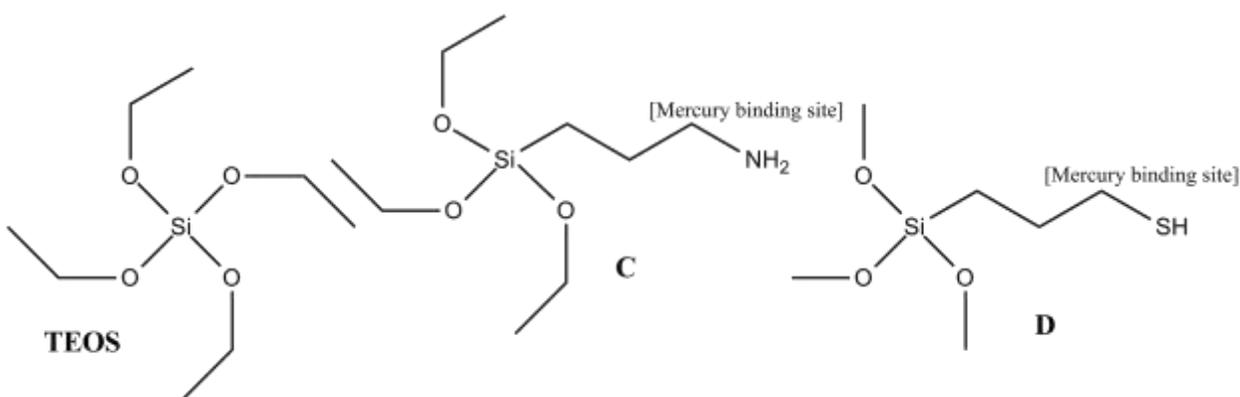


**Figure 1: The structure of the ligands. 3-mercaptopropionic acid, A, has a single mercapto group, and lipoic acid, B, has two sulfide groups, a dithioether. Both bind to the particles' oxide surfaces via the carboxylic acid group.**

---

Another method of using nanoparticles with binding ligands involves a silica shell. By using tetraethoxysilicate (TEOS), a thin silica shell can be formed on the surface of the.<sup>21</sup> Functionalized silicates have also been shown to bind  $\text{Hg}^{2+}$  ion in water.<sup>22</sup> Both silicates aminopropyltetrasilane (APTES) and mercaptopropyltrimethoxysilane (MPTMS) were shown to effectively bind  $\text{Hg}^{2+}$ ; APTES

was dependent upon pH, while MPTES remained bound to  $\text{Hg}^{2+}$  even under lower pH conditions. El-Nahhal *et. al.*<sup>23</sup> developed a simple method for preparing polysiloxane-immobilized thiol and thiol-amine ligands. As of yet, functionalized silicates have not been used to coat particles for  $\text{Hg}^{2+}$  ligation. This research will attempt to use both carboxylic acid chains with sulfur-containing groups and functionalized thiol-silicates to remediate  $\text{Hg}^{2+}$  from aqueous media. The structure of TEOS, APTES, and MPTMS are shown in Figure 2.



**Figure 2: The structure of the coating agent, TEOS, and the two organosilane ligands: APTES, C, and MPTMS, D. TEOS binds to the particles and the ligands via condensation reactions. APTES, C, contains an amine binding group while MPTMS, D, contains a thiol group.**

---

A problem arises, however, when attempting to use thiol groups to bind  $\text{Hg}^{2+}$  ion in water. Thiol groups are notorious for oxidizing into disulfides in water.<sup>24</sup> In order to keep the thiol groups from oxidizing, a weak reducing agent can be introduced into the solution. Dithiothreitol (DTT) has been shown to be an effective protecting group for thiols in aqueous media.<sup>25</sup> Therefore, this research will investigate the effectiveness of ligation in the presence and absence of weak reducing agents such as DTT.

To adequately test the ability of the functionalized particles to bind  $\text{Hg}^{2+}$ , a safe method must be employed so as to limit exposure to toxic  $\text{Hg}^{2+}$  compounds. Because A,

**C** and **D** contain propyl chains, the potential for toxic organo-mercury compounds to form cannot be ignored. Organic mercury compounds, most commonly occurring in methylmercury-contaminated fish/shellfish, can be ingested via inhalation, oral-ingestion, and dermal-absorption and present very serious threats to human health.<sup>26</sup> Vaporization techniques such as ICP-MS, however, provide the most sensitive and comprehensive detection methods. Other potential quantitative analysis methods include electrochemical analysis and fluorescence analysis. Anodic stripping voltammetry has been used for ultra-trace determination of  $\text{Hg}^{2+}$  and other toxic metal ions,<sup>27</sup> and cyclic square wave voltammetry can be used for adsorbed reactants.<sup>28</sup> There are several fluorophores that bind to  $\text{Hg}^{2+}$  and can be used to fluorescence analysis.<sup>29</sup> ICP-MS was used to analyze  $\text{Hg}^{2+}$  content in the water after nanoparticle exposure, because the concentrations of the sample solutions are extremely low; therefore, sensitivity is of utmost importance. Proper safety precautions were taken to minimize exposure to volatile Hg-containing compounds, such as dissolving Au-salt in the  $\text{Hg}^{2+}$  solutions to keep any free  $\text{Hg}^{2+}$  oxidized in its less-volatile, divalent species.

## CHAPTER 2

### MATERIALS & METHODS

#### Nanoparticle Synthesis

The aminolytic method was utilized in the synthesis of magnetic spinel ferrite nanoparticles.<sup>13</sup> To prepare the metal acetate necessary, 20 mmol of anhydrous  $\text{FeCl}_3$  (Alfa Aesar, 98%) and 10 mmol of either  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Alfa Aesar, 99.9%),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (FisherChemical, 99.9%), or  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (FisherChemical, 100.0%) were dissolved in 150 mL of deionized water in Erlenmeyer flask, resulting in an orange, transparent solution. Subsequently, 150 mL of 1M NaOH was added. The solution turned dark brown, and a precipitate formed. The resulting solution was stirred for 2 hours, then centrifuged at 50% full speed for 20 min 5 times, re-suspending the precipitate with deionized water after each centrifugation. The precipitate was dissolved in 40 mL of glacial acetic acid (J.T. Baker, 100%) and heated to 70 °C overnight, completing the metal acetate synthesis.

The metal acetate was ground into fine powder, 1.5 g of which was dissolved in 40 mL of  $\text{Bn}_2\text{O}$  (Alfa Aesar, 98+%) and 10 mL of oleylamine (TCI, >40%). The solution was prepared in a three-neck flask, in which a thermometer, condenser, and argon gas inlet were for the entirety of the reaction. The solution, upon complete dissolution, was heated to 140 °C for 1 h, then further heated to 240 °C for 1-2 h. A brown precipitate formed during the heating. Upon cooling to room temperature, the precipitate was collected with a large magnet and thoroughly washed with ethanol several times to remove the surfactant. The particles were allowed to dry overnight before being ground into a fine powder. The particles were characterized through X-ray diffraction (XRD), using a Philips X'pert, and Superconducting quantum interference (SQUID) hysteresis, using a Quantum Design MPMS-5S.

## Coating Methods

To coat the cobalt ferrites with the carboxylic acid ligands, the method developed by Vestal and Zhang<sup>20</sup> was modified for the ligands under investigation in this experiment. A 0.1 M solution of the ligand (A: Alpha Aesar, 99%; B: synth. by Gabriel Hernandez) in ethanol was prepared, and a sample of cobalt ferrites was added. The mixture was sealed and stirred overnight. After sufficient stirring, the particles were collecting with a strong magnet and washed several times with ethanol and all the supernatant residue was gone. The cobalt ferrites were allowed to dry overnight before being crushed into a fine powder and analyzed via XRD and XPS (ThermoK Alpha).

To coat the particles with the functionalized silicates, a 0.8 M ammonia and 6 M deionized water solution was prepared in 100mL of ethanol. To the solution, 200mg of the cobalt ferrite nanoparticles were added. A 0.46 M TEOS-ethanol (Alfa Aesar, 99+%) solution was added dropwise over 30-45 min. The solution was let stir for 30-45 min after complete TEOS addition, then 6 mL APTES (Alfa Aesar, 98%) or 4 mL MPTMS (Sigma-Aldrich, 95%) was added slowly. The solution was let stir for 10 h and let age for 5 h before the particles were isolated and washed with ethanol and water. The washed particles were dried in a vacuum oven (100 °C) for several hours before surface analysis via XPS.

## Remediation & Analysis

To test the ability of the functionalized particles to bind  $\text{Hg}^{2+}$ , an ICP-MS (Perkin-Elmer NexION 300) was used. A high-purity  $\text{Hg}^{2+}$  standard (Claritas PPT SPEX Certiprep 10ppm) was diluted to 1 ppb, 2 ppb, 3 ppb, 10 ppb, and 25 ppb in 10mL  $\text{H}_2\text{O}$  and 200 ppb  $\text{HNO}_3$  (Fisher Chemical, 69.0%-71.0%).  $\text{HAuCl}_4$  (Alpha Aesar, 99.9%) was added to stabilize the  $\text{Hg}^{2+}$  ions;  $\text{Hg}^{2+}$  can be reduced to more volatile forms, thus reducing the overall  $\text{Hg}^{2+}$  content in the standard solutions. These standard solutions were used to create a calibration curve. Functionalized particles samples were suspended in 100 ppb  $\text{Hg}^{2+}$  solutions for 30 minutes and separated with a strong magnet. The solution

was then analyzed via ICP-MS, and the remaining  $\text{Hg}^{2+}$  content was calculated from the calibration curve. Because thiols also bind Au strongly, the  $\text{HAuCl}_4$  was not added until after the particles were removed from the solution in order to stabilize the remaining  $\text{Hg}^{2+}$  ions.

To determine the optimal particle-solution density, five 20 mL samples of 50 ppb Hg were obtained using  $\text{HgCl}_2$  salt. A different amount of functionalized particles was exposed to each solution for 15-20 minutes and removed with a strong magnet. The solutions were then analyzed via ICP-MS. Using the optimal particle-solution density, the exposure time was varied to determine how quickly the particles remove  $\text{Hg}^{2+}$  ions below the ICP-MS detection limits. A 1000 mL solution of 50 ppb was sampled at intervals of 30 min, 1 h, 90 min, 2 h, 3 h, and 4 h. Each sample was analyzed via ICP-MS to determine when  $\text{Hg}^{2+}$  can no longer be detected or no significant decrease in  $\text{Hg}^{2+}$  concentration can be detected.

The ICP-MS results for each ligand were compared to determine the most effective method of  $\text{Hg}^{2+}$  removal. The particles were subsequently washed and dried. XPS and SQUID analyses were performed on the separated particles to determine if  $\text{Hg}^{2+}$  ions were present on the surface of the particles and to determine any change in the magnetic properties of the cobalt ferrites after coating, functionalization, and  $\text{Hg}^{2+}$  exposure.

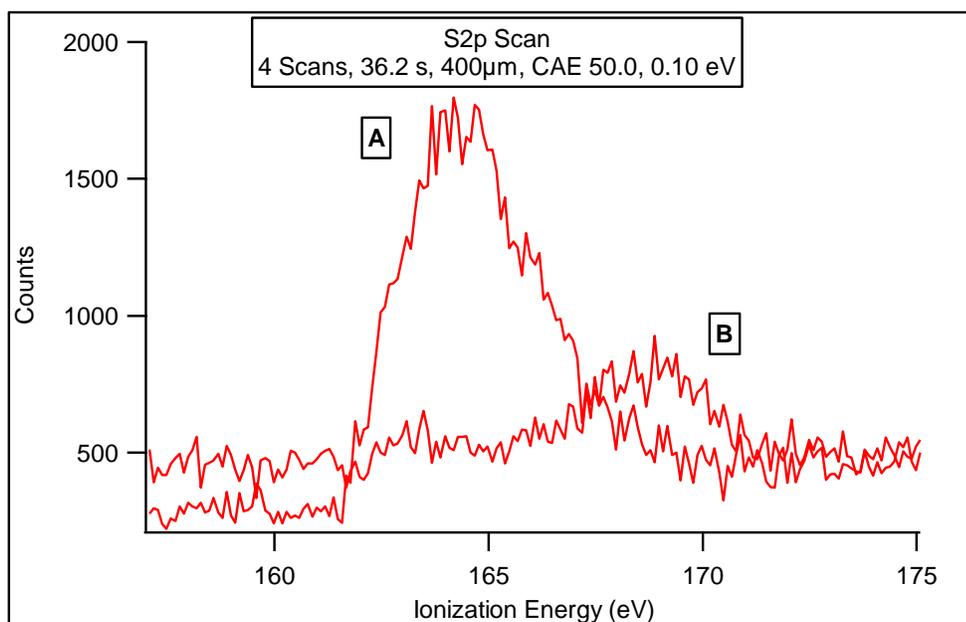
## CHAPTER 3

### RESULTS

#### Coating Confirmation via XPS

Coating the cobalt ferrites with 3-mercaptopropionic acid, **A**, was more successful than coating with lipoic acid, **B**. The XPS spectrum for **A** exhibited a pronounced peak of 1797 counts/s at 164.2 eV, while the spectrum for **B** exhibited no peaks of more than 1000 counts/s (Figure 3). It is peculiar that **A** bound better than **B** since both are binding via the same mechanism – a carboxylic group. Perhaps the ring on **B** caused too much steric hindrance between the cobalt ferrite and the carboxylic acid group. Nonetheless, **A** was chosen for the  $\text{Hg}^{2+}$  ligation experiments.

---

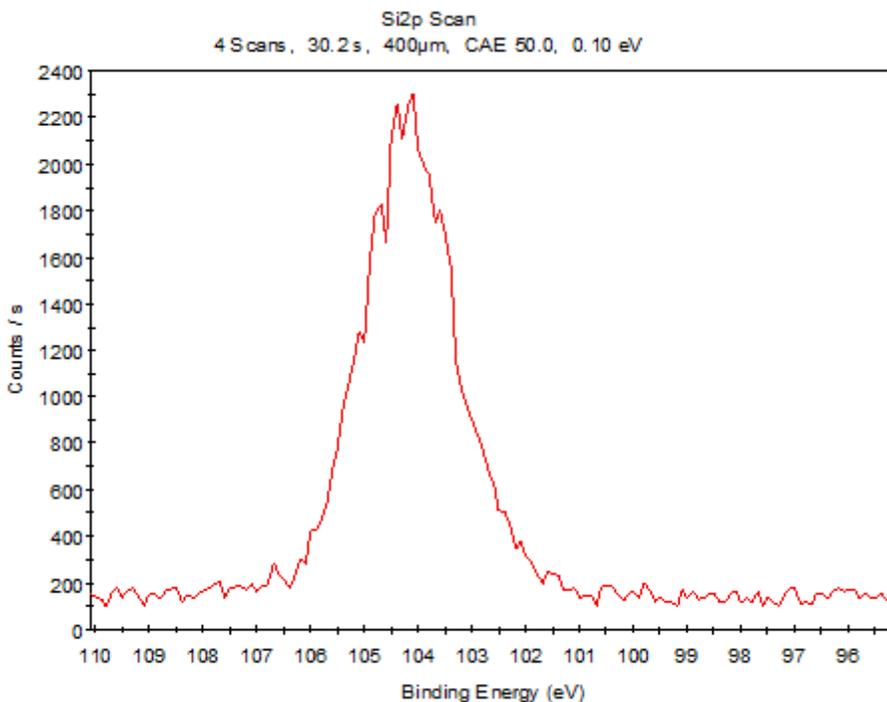


**Figure 3: The XPS spectrum for ligand coating trial 1. A = 3-mercaptopropionic acid, B = lipoic acid. A clearly bound to the cobalt ferrites better and was, thus, selected for the  $\text{Hg}^{2+}$  ligation experiment.**

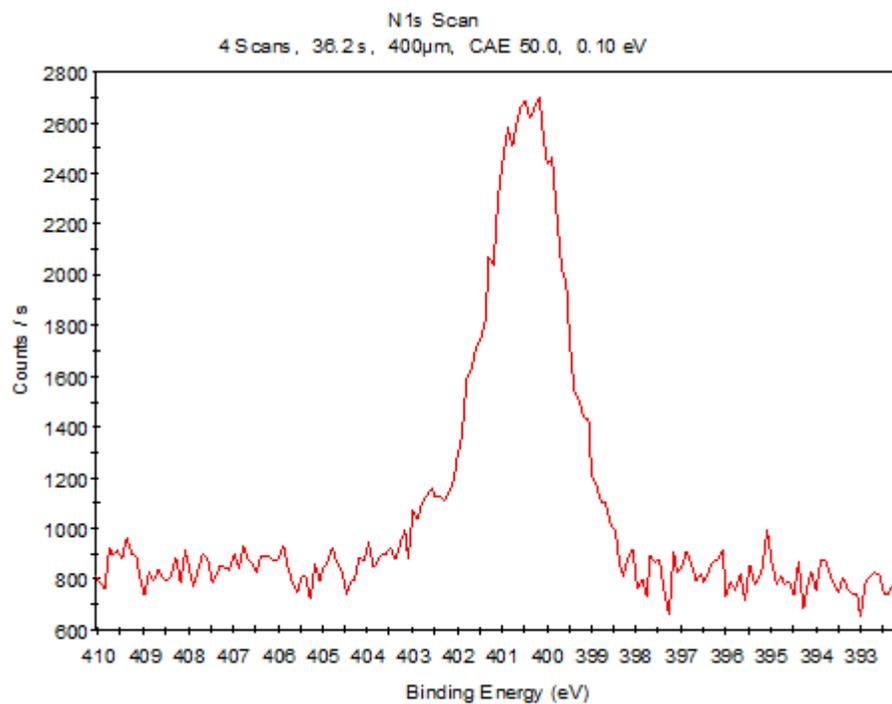
---

The preliminary XPS results from the silica coating method suggests the particles were successfully coated with a silica shell and functionalized with APTES, **C**, and MPTMS, **D**. Clear peaks exist in the silicon, nitrogen and sulfur binding energy (eV) ranges, as shown in Figures 4-6. The results are supported by those of Luo, Hong, *et. al.*<sup>22</sup> and El-Nahhal, *et. al.*<sup>24</sup> from whom the employed procedure was adapted to the cobalt ferrites.

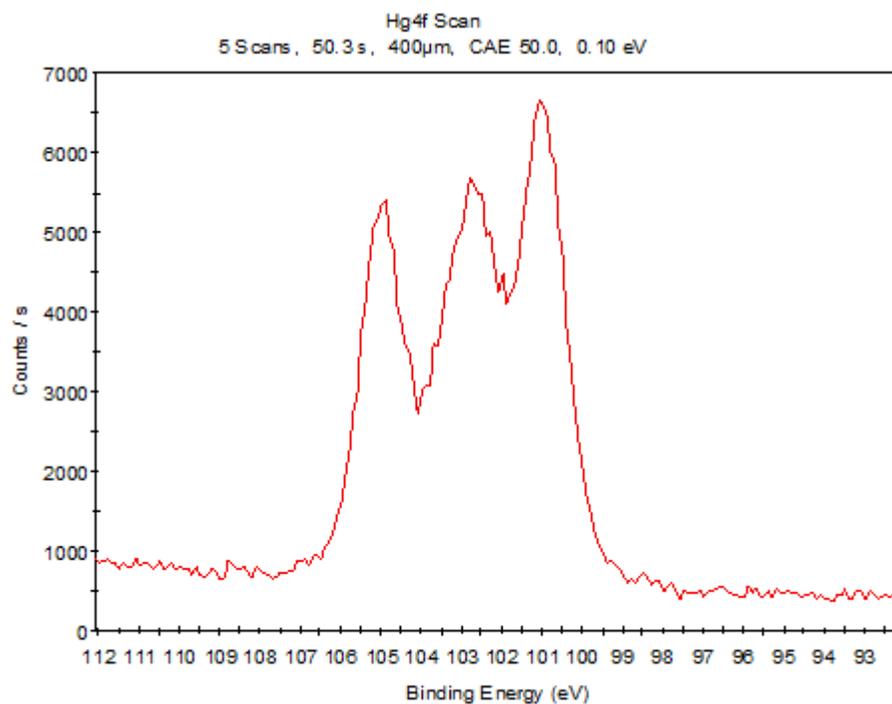
To determine whether the functionalized nanoparticles bind  $\text{Hg}^{2+}$  in water, a concentrated  $\text{Hg}^{2+}$  solution was prepared. A small sample of the functionalized nanoparticles were added to the solution and stirred overnight before isolating the nanoparticles with a strong magnet. The nanoparticles were washed, dried and analyzed via XPS. The XPS spectrum showed a significant peak in the Hg4f region of the XPS spectrum, confirming that the particles functionalized with **C** and **D** did bind  $\text{Hg}^{2+}$  in water. The Hg4f peak is shown in Figure 7.



**Figure 4: The silicon-2p peak suggests that particles were successfully coated with TEOS.**



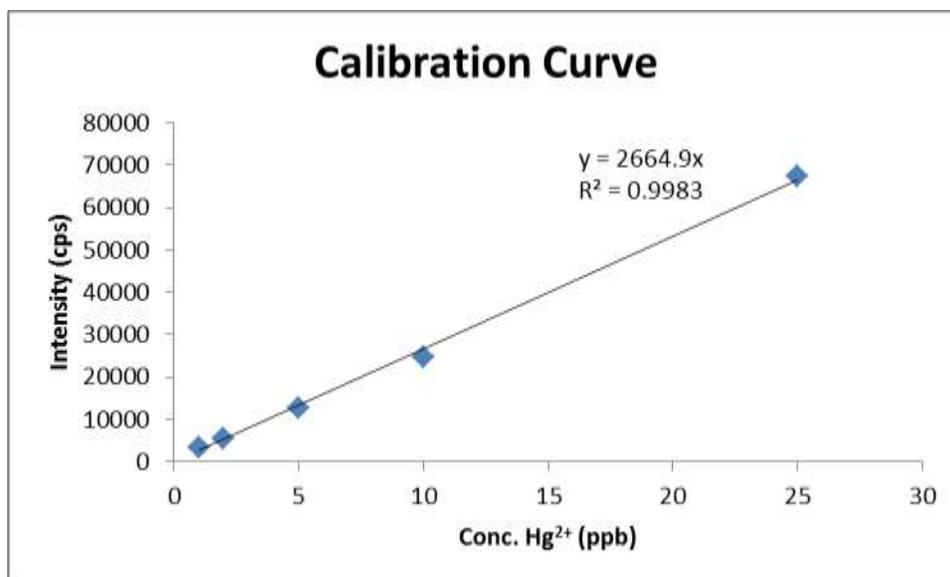
**Figure 5: The nitrogen-1s peak suggests that surface of the silica shell was successfully functionalized with APTES.**



**Figure 7: The Hg4f region in the XPS spectrum shows significant peaks, suggesting Hg<sup>2+</sup> was successfully separated from the original solution.**

## Remediation Analysis via ICP-MS

Thus far, only the particles functionalized with **A** were used for the remediation experiment. To determine the binding efficiency of the nanoparticles functionalized with **A** 50 ppb  $\text{Hg}^{2+}$  solutions and analyzed via ICP-MS. A calibration curve was obtained using high-purity  $\text{Hg}^{2+}$  standards, as shown in Figure 9. Remaining  $\text{Hg}^{2+}$ , percent removed and percent remaining after exposure to the functionalized particles is tabulated in Table 1. **A** removed, on average, 94.03% of  $\text{Hg}^{2+}$  in the solutions (Table 1).



**Figure 8:** The calibration curve for the  $\text{Hg}^{2+}$  standards exhibited a linear relationship as expected and enable the concentrations to be calculated.

**Table 1:** ICP-MS data showing  $\text{Hg}^{2+}$  removal and percent remaining  $\text{Hg}^{2+}$ .

Ligand	Trial	$\text{Hg}^{2+}$ (ppb)	Avg.	% Removed	% Remaining
<b>A</b>	1	3.81	3.648575	92.38	7.62
	2	3.49		93.03	6.97
	3	1.65		96.70	3.30

The initial remediation trials were conducted at constant mass-of-particles-to-volume-solution ratio and a constant time of exposure. The minimum density of particles

needed (mg/L) to remediate 90+% of the  $\text{Hg}^{2+}$  ion in solution was investigated by varying the mass of particles in solution while the volume is held constant. The concentration of  $\text{Hg}^{2+}$  and exposure time were also held constant. Five different 20 mL solutions of 50 ppb  $\text{Hg}^{2+}$  were exposed to masses of 5 mg, 10 mg, 20 mg, 30 mg and 40 mg of particles functionalized with **A** for 30 minutes (Table 2). The results showed the expected trend – as the density of the particles in solution increased, the amount of  $\text{Hg}^{2+}$  removed increased (Figure 9, Table 2).

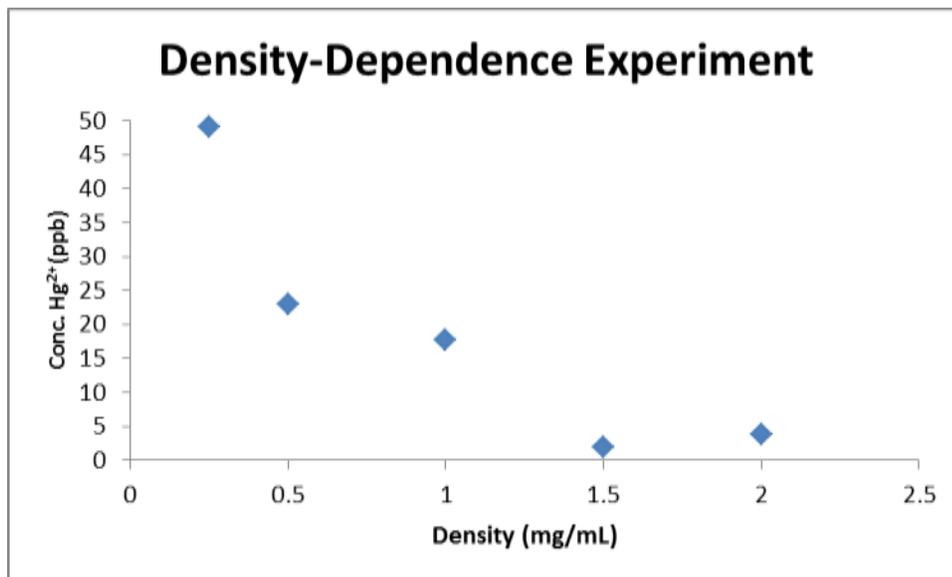
For the exposure-time experiment a 500 mL, 50 ppb  $\text{Hg}^{2+}$  solution of density 1.00 mg/mL was obtained and sampled at time intervals of 30 min, 60 min, 90 min, 120 min, 180 min and 240 min (Table 3). 10 mL aliquots were sampled and analyzed via ICP-MS. The change in the particle-solution density due to the sampling was minimal. The results exhibited a decrease in  $\text{Hg}^{2+}$  concentration over time, except for the last sample, which showed an insignificant increase in  $\text{Hg}^{2+}$  concentration, possibly due to insufficient cleaning of the glassware used to sample (Figure 10, Table 3).

---

**Table 2: Density-dependence experiment structure and results.**

Sample #	Mass particles (mg)	Volume solution (mL)	Density (mg/mL)	$\text{Hg}^{2+}$ (ppb)
1	5	20	0.25	*49.01
2	10	20	0.50	*23.00
3	20	20	1.00	17.66
4	30	20	1.50	1.81
5	40	20	2.00	3.80

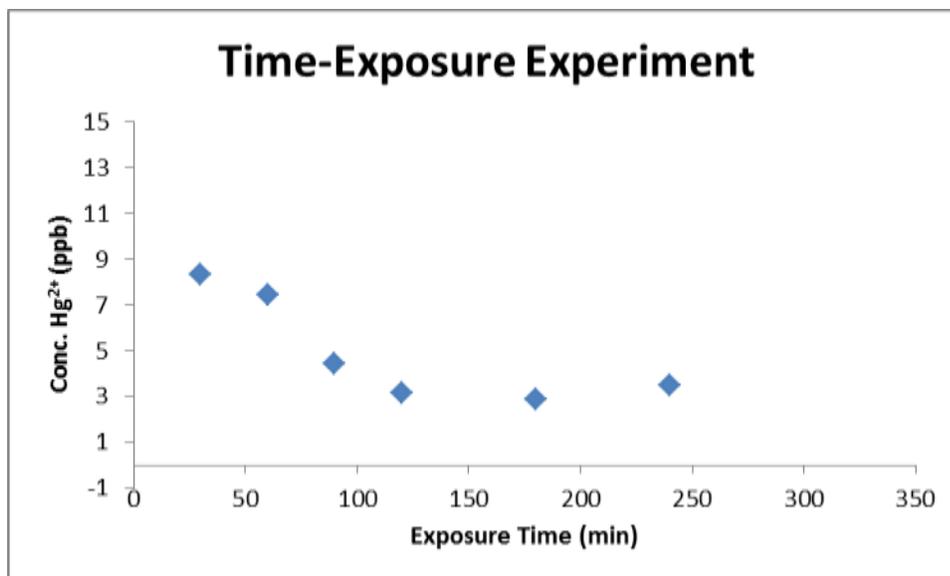
\* Samples 1 and 2 were outside of the calibration curve range.



**Figure 9:** Graphed results from the density-dependence experiment. The Hg<sup>2+</sup> concentration decreased as the density increased.

**Table 3:** Exposure-time experiment structure and results.

Sample	Exposure time (min)	Vol. remaining (mL)	Hg (ppb)
1	30	490	8.323764
2	60	480	7.450186
3	90	470	4.460955
4	120	460	3.137829
5	180	450	2.878157
6	240	440	3.4718



**Figure 9: Graphed results from the exposure-time experiment. The Hg<sup>2+</sup> concentration decreased as time progressed.**

## CHAPTER 4

### FUTURE WORK

While the cobalt ferrites functionalized with ligand **A** were shown to remove high levels  $\text{Hg}^{2+}$  ions from solution, ligands **C** and **D** also need to be investigated. The results from the remaining two ligands will be compared to those of **A**. The density-dependence and exposure-time experiments need also be performed for both **C** and **D** for comparison to the results with **A**. Proposed experimental procedures are shown in Tables 3- 5.

**Table 4: Proposed  $\text{Hg}^{2+}$  removal experiment with ligands C and D.**

Sample	Ligand	Mass p. (mg)	Vol. Sol. (mL)	Density (g/L)	Time (min)
1	C	40	20	2	30
2	C	40	20	2	30
3	C	40	20	2	30
1	D	40	20	2	30
2	D	40	20	2	30
3	D	40	20	2	30

**Table 5: Proposed density-dependence experiment to determine optimal particle-solution density for  $\text{Hg}^{2+}$  removal with ligands C and D.**

Trial	Ligand	Mass p. (mg)	$\text{Hg}^{2+}$ conc. (ppb)	Vol. Sol. (mL)	Density (mg/mL)
1	C	5	50	20	0.25
2	C	10	50	20	0.5
3	C	20	50	20	1
4	C	30	50	20	1.5
5	C	40	50	20	2
1	D	5	50	20	0.25
2	D	10	50	20	0.5
3	D	20	50	20	1
4	D	30	50	20	1.5
5	D	40	50	20	2

**Table 6: Proposed exposure-time experiment to determine the optimal particle-solution density for Hg<sup>2+</sup> removal with ligands C and D.**

Trial	Ligand	Vol. Remaining (mL)	Density (mg/L)	Exposure Time (min)
1	C	490	*optimized	30
2	C	480	*optimized	60
3	C	470	*optimized	90
4	C	460	*optimized	120
5	C	450	*optimized	180
6	C	440	*optimized	240
1	D	490	*optimized	30
2	D	480	*optimized	60
3	D	470	*optimized	90
4	D	460	*optimized	120
5	D	450	*optimized	180
6	D	440	*optimized	240

**\*The optimized density will be determined from the density-dependence experiment.**

We are hoping to completely optimize the Hg<sup>2+</sup> removal method. In doing so, the most economical approach to removing Hg<sup>2+</sup> will be determined, showing that functionalized magnetic nanoparticles are a viable separations methods with far-reaching applications. We will also investigate methods with which we can recycle the coated cobalt ferrites, such as leaching the Hg<sup>2+</sup> off under harshly acidic conditions. The problem arises, however, of what to do with the very acidic, concentrated Hg<sup>2+</sup> solution that results from the leaching. Nonetheless, recyclable methods will be investigated to determine if it is feasible to reuse the coated particles, making the method even more economical.

The ease with which both carboxylic acid ligands and functionalized silicates were coated onto the cobalt ferrite surface opens up future research that targets other toxins. Ion-selective ligands and chelators can be bound to ferrite nanoparticles in order to target certain heavy-metal ions and radioactive isotopes; the same is true for

functionalized silicates. Little research has been conducted with coated magnetic nanoparticles already<sup>30</sup>, and future work will add to the field. Functionalizing well-known heavy metal chelators, such as EDTA, with long carboxylic acid chains or organosilicate groups could enable the chelators to be coated onto the surface of cobalt ferrite nanoparticles and, thus, used to separate the heavy metals from solution. Our future work will investigate the possibility to extend our successes with Hg<sup>2+</sup> removal to other environmental toxins.

## REFERENCES

- [1] Manahan, S. E. *Environmental Chemistry*. Lewis Publishers: Boca Raton, FL, 1994.
- [2] Dorea, J. G. *Ecotoxicol. Environ. Saf.* **2004**, 57, 248-56.
- [3] Rofouei, Mohammad K.; Rezaei, A.; Masteri-Farahani, M.; Khani, H. *Anal. Meth.* **2012**, 959-966.
- [4] Campos, A. F. C.; Ferreira, M. A.; Marinho, E. P.; Tourinho, F. A.; Depeyrot, J. *Phys. Procedia* **2010**, 9, 45-48.
- [5] Drexler, K. E. *PNAS.* **1981**, 78, 5275-8.
- [6] Lu, A.-H.; Salabas, E. L.; Schüth, F. *Angew. Chem.* **2007**, 46, 1222-44.
- [7] Green, D. J.; Halloran, J.; Johnson, D. W.; Klein, L. *Jo. Am. Chem. Soc.* **2011**, 25.
- [8] Han, Man H. Diss. Georgia Institute of Technology, *2009 Georgia Tech Theses and Dissertations*. School of Chemistry and Biochemistry, Dec. 2008.
- [9] Zhang, Z. L.; Guo, L.; Wang, W. D. *J. Mater. Res.* **2001**, 16, 803-5.
- [10] Ye, C. H.; Wang, G. Y.; Kong, M. G.; Zhang, L. D. *J. Nanomater.* **2006**, 1.
- [11] Zhang, J. R.; Gao, L. *Mater. Chem. Phys.* **2004**, 87, 10-3.
- [12] Liu, Y. P.; Zhang, Y. H.; Zhang, M. W.; Xhang, W. H.; Qian, Y. T.; Yang, L.; Wang, C. S.; Chen, Z. W.; *Mater. Sci. Eng.* **1997**, 49, 42-5.
- [13] Stone, C. A.; Linhardt, L. A.; Zhang, Z. J. *Abstracts*, 60th Southeast Regional Meeting of the American Chemical Society, Nashville, TN, November 12-15, 2008.
- [14] United States Environmental Protection Agency. National Recommended Water Quality Criteria.  
<http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm>.
- [15] Luo, W., Wang, T., Jiao, W., Hu, W., Naile, J. E., Khim, J. S., Giesy, J. P., et al. *J. Hazard. Mater.* **2012**, 215-216, 199-207.
- [16] Rofouei, M. K.; Rezaei, A.; Masteri-Farahani, M.; Khani, H. *Anal. Meth.* **2012**, 959-966.
- [17] Campos, A. F. C.; Ferreira, M. A.; Marinho, E. P.; Tourinho, F. A.; Depeyrot, J. *Phys. Procedia* **2010**, 9, 45-48

- [18] Figueira, P.; Lopes, C. B.; Daniel-da-Silva, A. L.; Pereira, E.; Duarte, A. C.; Trindade, T. *Water Res.*, **2011**, *45*, 5773–84.
- [19] Colvin, V. L.; Goldstein, A. N.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1992**, *114*, 5221.
- [20] Vestal, C. R.; Zhang, Z. J. *Nano Lett.* **2003**, *3*, 1739–1743.
- [21] Luo, Z.; Hong, R. Y.; Xie, H. D.; Feng, W. G. *Powder Technol.* **2012**, *281*, 23-30.
- [22] Walcarius, Alain; Etienne, Mathieu; Delacote, Cyril. *Anal. Chim. Acta.* **2004**, *508*, 97-98.
- [23] El-Nahhal, I. M.; Yang, J. J.; Chuang, I.; Maciel, G. E. *J. Non-Cryst. Solids.* **1996**, *208*, 105-18.
- [24] Chakraborty, M.; Mandal, P. C.; Mukhopadhyay, S. *Polyhedron.* **2012**, *45*, 213–220.
- [25] Cleland, W. W. *Biochem.* **1963**, *3*, 480-2.
- [26] Richer, J. F.; Murray, H. E.; Prince, G. R. *Toxicol. Ind. Health.* **2002**, *18*, 109-60.
- [27] Locatelli, C.; Melucci, D. *Cent.Eur. J. Chem.* **2013**, *11*, 790-800.
- [28] Damm, M. A.; Bottomley, L. A. *Abstracts of Papers*, 241<sup>st</sup> ACS National Meeting & Exposition, Anaheim, CA, March 27-31, 2011.
- [29] Wuo, Z.; Zhu, W.; Shen, L.; Tian, H. *Angew. Chem.* **2007**, *46*, 5549-5553.
- [30] Kaur, M.; Han, H.; Paszczynski, A.; Kaczor, J.; Qiang, Y.; Johnson, A. *Abstracts*, 65<sup>th</sup> Northwest and 22<sup>ns</sup> Rocky Mountain Regional Meeting of the American Chemical Society, Pullman, WA, June 20-23, 2010.