

MERCURY REMOVAL FROM AQUEOUS SYSTEMS USING COMMERCIAL  
AND LABORATORY PREPARED METAL OXIDE NANOPARTICLES

A Thesis

by

ISHAN DESAI

Submitted to the Office of Graduate Studies of  
Texas A&M University  
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2009

Major Subject: Civil Engineering

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Approved by:

Chair of Committee,	Bryan Boulanger
Committee Members,	Bill Batchelor
	Raghupathy Karthikeyan
Head of Department,	David Rosowsky

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## ABSTRACT

Mercury Removal from Aqueous Systems Using Commercial and Laboratory Prepared Metal Oxide Nanoparticles. (August 2009)

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Chair of Advisory Committee: Dr. Bryan Boulanger

Five commercial metal oxide nanoparticles (CuO, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) have been individually screened for mercury removal in a batch reactor under bicarbonate buffered and non-buffered aqueous solutions (DI water). Copper oxide was then selected for surface modification to enhance mercury removal. The surfaces of both laboratory prepared and commercially available copper oxide nanoparticles were treated with 1-octanethiol to produce copper sulfide and/or copper alkanethiol nanoparticles. The resulting particles were characterized using X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The novel nanoparticles demonstrated very high mercury removal (> 99%) from both the buffered and non-buffered aqueous solutions.

To my family

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## CHAPTER I

### INTRODUCTION

#### A. Background

The presence of mercury (Hg) in aquatic systems is a major threat to human health and the environment because it imparts both acute and chronic toxicity at low dosage levels. Significant regional pollution of mercury was historically caused by the release of mercury into the environment from mining, industrial applications, and energy generation. The major ore of mercury is cinnabar (mercuric sulfide) and it, was and is currently processed to meet the global demand. Mercurys use in chlor-alkali manufacturing; in the electrical, pharmaceutical, paper, pulp, and plastic industry; and in agricultural activities has lead to widespread contamination of air, sediment, soil, and water.

According to a 2002 United Nations Environmental Program report, the primary releases of mercury to the environment are due to 1) mobilization of naturally occurring mercury, 2) human activities causing release of mercury into the environment mainly by burning of fossil fuels, 3) use of mercury in various products and processes, and 4) re-mobilization of deposited mercury in soils, sediments and water [1]. Because of its hazardous nature and carcinogenicity, the United States (US) Environmental Protection Agency has set a drinking water limit of 2 parts-per-billion (ppb) for mercury. The US Food and Drug Administration has also set a 1 parts-per-million (ppm) limit in seafood. Legislation protecting water and food sources from mercury contamination is found in countries throughout the world. The mercury standards for drinking water adopted by EU countries, India and Canada is 1 ppb.

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Because mercury (as with other metals) cannot be destroyed, mercury released in our industrial past keeps re-circulating between environmental matrices. Long range transport of the circulating mercury has caused global contamination, which poses ecological and potential human health risk far away from known point sources.

Mercury, in its purist form, exists as a liquid at room temperature. In aquatic systems, mercury primarily exists in three states:  $\text{Hg}^0$  (metallic),  $\text{Hg}_2^{2+}$  (mercurous) and  $\text{Hg}^{2+}$  (mercuric) [2]. It exists both in inorganic, as well as organic forms. In aquatic systems, mercury also readily complexes with carbon in order to form organo-metallic compounds. Arguably the most important organo-metallic form of mercury is methyl mercury, which is known for its toxicity and its ability to bioaccumulate. The exact mercury species and complexes that exist in a given environment are dependent upon the conditions of the system.

As with all metals, the toxicity of mercury depends on the speciation and complexation of mercury found in the environment. However, the impact of all forms of mercury on the human body is well documented: mercury exposure results in systemic toxicity. Mercury affects the central nervous system ; may result in permanent damage of the brain and kidneys ; can significantly affect fetal growth during pregnancy ; and causes cardiovascular symptoms [3]. Because of its ability to bioaccumulate, methyl-mercury can increase in concentration within tissues as the trophic levels increase, resulting in a greater biological impact. Therefore, removing mercury from aquatic systems protects both ecological health and human health.

## B. Mercury Treatment Technologies in Use Today

Several technologies exist today for the removal of mercury from mercury contaminated water. Among the most common physical-chemical approaches used in mercury

treatment technologies are precipitation, coagulation/co-precipitation, and sorption (to activated carbon). Ion-exchange, chemical reduction, membrane separation, and microemulsion liquid membrane extraction are additional treatment schemes that are less commonly used. When deciding upon a treatment technology to remove mercury from environmental systems, the technology's performance, secondary waste generation, and economics must be taken into account. Each process based treatment technique is briefly discussed in the following paragraphs.

### 1. Precipitation

Precipitation techniques for mercury removal are the most commonly referenced and presented in the literature. However, precipitation of mercury has a major drawback - this process generates excess sulfide wastes that cause difficulties for handling, transporting, and disposing of the final reaction products. Mercury in these secondary products can resolubilize under the right conditions and result in pollution at other locations [4].

### 2. Coagulation/Co-precipitation

Coagulation and co-precipitation techniques result in lower levels of mercury removal compared to the other mentioned processes, but are inexpensive. Among the co-precipitation techniques the most common coagulants that have been employed are alum, iron and lime. The main mechanism for mercury removal reported here is adsorption co-precipitation. Mercury is adsorbed in the aluminum hydroxide or the iron hydroxide bulk solid formed as the case may be. Similar to precipitation-based techniques, the mercury adsorbed can re-solubilize in the solution posing a potential problem for handling, transportation, and final disposal [4].

### 3. Ion Exchange

Ion exchange based technologies demonstrate high mercury removal rates, but many ion exchange resins have poor mechanical strength. In ion exchange based technologies, the resins are typically employed as packed columns that mercury contaminated water flows through. Anionic resins have been mainly employed for the removal of cationic mercury from waste streams, but recently some cationic resins have also been reported. A cationic resin having a thiol group has been observed to remove ionic mercury. Chelate resins having high mercury removal capacity have also been reported. These resins have complex molecular structures where the metal can attach to the structure forming a ring or chelate. The main disadvantage of this process is that it can lead to inconsistent effluent concentrations and this process cannot be employed in cases where there is a high dissolved solid content. Additionally, some types of ion exchange resins are easily oxidized leading to a reduction in their longevity [4].

### 4. Chemical Reduction

Chemical reduction based technologies use metal or metal complexes that are higher in the electromotive series to reduce mercury. The most common reducing agents that have been used are Al, Zn, Fe,  $\text{N}_2\text{H}_4$ ,  $\text{SnCl}_2$ , and  $\text{NaBH}_4$ . The major drawback for this process is that it leads to generation of secondary wastes that cause concerns in handling, transport, and final disposal [4].

### 5. Membrane Separation

Membrane based separation technologies, such as ultrafiltration, charged filtration, cross flow microfiltration, magnetic filtration, and reverse osmosis have also been demonstrated to successfully remove mercury from contaminated water. Membrane

filtration (ultrafiltration (UF), microfiltration (MF), and reverse osmosis(RO)) separates particles based upon size exclusion using a pressure gradient to remove the particles across a membrane. In case of charged filtration the membrane used (UF,MF,RO) is negatively charged which minimizes fouling of the membrane. The cross flow microfiltration process uses a moving membrane for the purpose of filtration. In both ultrafiltration and cross flow microfiltration, pre-treatment of the process feed containing mercury is required as these processes cannot remove the mercury alone in solution based upon size exclusion. Magnetic filtration first creates an insoluble magnetic mercury based precipitate that is removed from solution when the precipitate is passed through ferro-magnetic wires with an applied magnetic field. In microemulsion liquid membrane technologies, a microemulsion is first formed by the addition of oleic acid tetradecane, DNP-8 surfactant, and 6N sulfuric acid to mercury contaminated water. Membrane separation of the resulting microemulsion leads to two phases: an aqueous phase and an emulsion phase. Demulsifying the resulting aqueous phase creates a secondary waste stream that is rich in mercury. The main drawbacks of membrane separation technologies for the removal of mercury are 1) they involve multiple steps, 2) operate at high pressure and cost, 3) produce secondary waste streams, and 4) eventually foul [4].

## 6. Adsorption

Adsorption based technologies are the most prominently used technologies for the removal of mercury because of their efficient removal capacity and overall low cost. Adsorbents also can potentially be regenerated further adding to cost savings. Adsorbents shown to remove mercury include activated carbon [5],[6], bicarbonate-treated peanut hull carbon [7], modified *Hardwickia binata* bark [8], coal fly ash [9],onion skin [10], waste rubber [11],rice husk [12],fertilizer waste slurry [13], photo film waste

sludge, jackfruit peel, coir pith [14], flax shive [15], exhausted coffee grounds [16], walnut shell [17], papaya [18] and sago waste [19]. A number of sulfur based adsorbents have also been reported in the literature because of their affinity for mercury. The Pacific Northwest National Laboratory synthesized adsorbents consisting of self-assembled mercaptan groups on silica (SAMMS) also have high affinity for mercury [20]. Their hydrophobic and hydrophilic groups can be altered to target specific contaminants for removal. In addition to SAMMS, polymers that have surface bound ligands, which can bind with metals, have been developed in recent years. Amide compounds are one such ligand that demonstrate high affinity for mercury. Cross linked polyacrylamide, therefore, is another potent sorbent for mercury removal [21].

## 7. Additional Miscellaneous Technologies

Thermal treatment is sometimes used to remove mercury from water. In thermal treatment, the contaminated water is heated and the resulting vaporized mercury is collected and condensed. Chemical leaching is another method demonstrated to remove mercury. In chemical leaching, leaching solutions such as nitric acid, hypochlorous acid, and sulfuric acid are added into mercury contaminated water. The chemical leaching procedure has been applied to treat elemental and inorganic mercury containing waters. Electrolytic methods have also been employed where the electric current passes to convert the metals into stable metal oxides. Stabilization and amalgamation are two other processes to convert mercury into an immobile form and reducing mercury leaching into the environment from contaminated sites. Physical separation takes advantage of the fact that mercury has high density compared to other materials. This method is capable of directly removing unbound mercury. Finally, in addition to the aforementioned physical and chemical based processes, it is now known that certain bacteria and plants have the ability to assimilate mercury.



However, such biological processes take place at a very slow pace and are likely only reasonable for natural monitored attenuation [21]. Various nanoscale technologies also demonstrate promise in removing mercury from aqueous systems. While the use of nanotechnology to remove mercury is still limited to laboratory research, as the cost of nanotechnology continues to decrease the use of nanotechnology for mercury removal at the field scale will grow.

### C. Nanotechnology and Mercury Removal

There has been a growing need for a technology that has low overall cost, durability, and is more effective than the current options. Nanotechnology offers promising potential for removing mercury from contaminated water and wastewater quickly, efficiently, and at lower future costs. Nanotechnology is the engineering and art of manipulating matter at the nanoscale (1-100 nm). Several nano-based technologies are currently under investigation for the removal of contaminants (including mercury) from water. The two most common technologies involve nanoparticles and nanoporous sorbents.

#### 1. Nanoporous Sorbents

Novel nanoporous sorbents have been synthesized by both public and private sectors. These nanoporous sorbent materials consist of mesoporous ceramic supports with monolayers of molecules on the surface. Both the support and the monolayer can be tailored according to the contaminant being removed. The advantage of nanosorbents is that they have an extremely high surface area (  $1000\text{m}^2/\text{g}$ ) to mass ratio. Nanoporous supports are prepared by both precipitation and molecular assembly based techniques. The result of the process is a micellar structure with an oxide layer

precipitated on it. Subsequent calcinations result in highly porous supports. Molecular assembly is the process where a functional group is aligned with the active sites of the surface of the sorbent. The functional group consists of a hydrophilic head and a hydrophobic tail. The head and the tail group can be tailored according to the type of the contaminant to be removed. In case of mercury removal alkylthiols are chosen as the functional group for the head as they have very high affinity for mercury [21],[22].

## 2. Nanoparticles

Metal-oxide nanoparticles, in particular, have been widely evaluated for the removal of various contaminants from water. Their large surface area and higher reactivity makes them an ideal choice for removal of contaminants. Iron-oxides, for instance, have been widely employed for the removal of arsenic. The other oxides which have shown promising results for arsenic removal include the nanoparticles of copper oxide [23], titanium dioxide [24],[25],[26],iron-titanium binary mixed oxide [27], humic acid coated iron oxide [28] and cerium doped iron oxide [29]. Successful attempts have been also made to remove chromium (using nanoscale surface modified jacobsite [30], maghemite [31], akaganeite [32]), lead (using nanoscale titanium dioxide [33], zero-valent iron [34] and nanoscale chitosan [35]), cadmium (using nanoscale modified titanium dioxide[36]), perchlorates and nitrates (both using nanoscale iron oxides [37]), [38],[39],[40],[41].Recent reports have shown mercury removal from aqueous systems through mackinawite [42], thiol based silica nanoparticles [43] and arginine modified titanium dioxide nanoparticles [44]. Alumina nanoparticles have also shown promising results in the removal of mercury [45].

#### D. Objectives of Thesis Research

The goal of this research was to create a metal oxide based nanoparticle with higher aqueous mercury removal efficiency than existing commercially available nanoparticles. Two objectives were established in order to meet the proposed goal. The objectives, along with the aims required to meet the objectives, are presented below.

**Objective 1** Evaluate commercial nanoparticles for their ability to remove mercury from contaminated water samples

**Aim 1** Develop laboratory techniques to work with nanoparticles

**Aim 2** Investigate mercury removal using commercial metal oxide nanoparticles

**Aim 3** Evaluate mercury removal by industrial resin

**Objective 2** Create a novel nanoparticle to increase mercury removal observed by commercial nanoparticles

**Aim 4** Create nanoparticles with sulfur amended surface functional groups

**Aim 5** Characterize the newly created nanoparticles

**Aim 6** Evaluate mercury removal by novel nanoparticles

The presented research evaluates mercury removal from laboratory-prepared buffered and non-buffered aqueous solutions by five commercial nanoparticles and a novel surface functionalized nanoparticle created and characterized in this research. The resulting effort provides insight into the future of mercury removal using nanoparticles and presents a simple way of surface amending nanoparticles to increase performance.

## CHAPTER II

### EXPERIMENTAL METHODS

#### A. Materials

Nanoparticles of aluminum oxide ( $< 50\text{nm}$ ), titanium(IV) oxide - anatase ( $< 25\text{ nm}$ ), iron(III) oxide ( $< 50\text{nm}$ ), silicon dioxide ( $10\text{-}20\text{nm}$ ), copper ( $< 50\text{nm}$ ), and copper oxide ( $< 50\text{nm}$ ) were purchased from Sigma-Aldrich (St Louis, USA). A highly selective resin (DOW XUS 43604.00,  $500\text{--}650\mu\text{m}$ ) designed to remove mercury is obtained from Dow Chemicals (Bellefonte, USA). Sodium borohydride ( $\text{NaBH}_4$ , 98% ACROS (New Jersey, USA)), hydrochloric acid (HCl, Mallinckrodt Chemicals (Phillipsburg, USA)), sodium hydroxide (NaOH, 97% Sigma-Aldrich (St Louis, USA)), Copper(II) acetate hydrate (Aldrich (St Louis, USA)), glacial acetic acid (99.5%, Fischer Scientific (Pittsburg, USA)), ethanol (99.5%, Sigma Aldrich (St Louis, USA)) were used as received. Water was purified using a Barnstead Nanopure Water system ( $> 17.7\text{ M}\Omega$ ).

#### B. Reaction System

A  $2\text{g/L}$  solution of each nanoparticle and resin was prepared in both Nano-pure water (non-buffered solution) and Nano-pure water buffered with  $10\text{mM NaHCO}_3$  (buffered solution). A  $200\text{ppb Hg}^{2+}$  solution was similarly prepared in both buffered and non-buffered solutions. A  $5\text{ mL}$  aliquot from an individual nanoparticle solution was mixed with  $5\text{ mL}$  of the mercury solution to create both buffered and non-buffered reaction vessels with a nanoparticle concentration of  $1\text{g/L}$  and a mercury concentration of  $100\text{ ppb}$ . Each prepared nanoparticle/mercury mixture was placed on a rotator for a period of  $24\text{ hrs}$ . It was assumed that the reaction reaches equilibrium in the given

time.

To evaluate mercury removal, after 24 hours of shaking the mixture, the mixture (both buffered and non-buffered) was placed inside microcentrifuge tubes. The microcentrifuge tubes were then positioned in a microcentrifuge and centrifuged for 40 minutes at a speed of 16,000 rpm. Following centrifugation, the supernatant within each microcentrifuge tube was collected in a separate container and analyzed using an atomic absorption spectrometer.

### C. Mercury Analysis

Mercury was analyzed using a Solar M6 Atomic Absorption Spectrometer which also has the V90 continuous hydride generator (Thermo Elemental) attached to it. The mercury analysis was based on the standard method 3112A for metal analysis by cold-vapor atomic absorption spectrometry. The percentage removal of mercury is calculated by measuring the mercury concentration before and after the reaction using the spectrometer.

### D. Creating Novel Surface Amended Copper Oxide Nanoparticles

Copper oxide nanoparticles have been synthesized using many different methods, including sol-gel [46], precipitation [47], electrochemical [48]; solid-state reaction [49]; alcohothermal [50]; microwave irradiation [51]; and thermal decomposition (green pathway) routes [52]. In this study, copper oxide nanoparticles have been prepared in the laboratory according to a method reported by Zhu et al.

The Zhu et al. method involves mixing 0.02M copper acetate solution with 1 mL glacial acetic acid while heating the mixture to 100°C. NaOH is then added to the solution at this temperature and an immediate black precipitate is obtained.

The solution is allowed to cool to room temperature and the precipitate is collected using a centrifuge. The precipitate is then heated to boil off the remaining solution under vacuum in order to obtain the copper oxide nanoparticles. The copper oxide nanoparticles are washed with distilled water and then with ethanol. The washed particles are then dried under vacuum.

Finally, both the laboratory prepared and commercial copper oxide nanoparticles were coated with 1-octanethiol to modify the surface with sulfur based functional groups. The modification is performed by reacting 0.2 g of each nanoparticle with 10 ml of 1-octanethiol in a flat bottom reaction flask. The mixture is then rapidly mixed for 10 minutes and heated under vacuum to vaporize off the octanethiol, resulting in a black precipitate.

#### E. Nanoparticle Characterization

The coated commercial and laboratory prepared nanoparticles were characterized using X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Energy-dispersive X-Ray fluorescence (EDXRF) analysis was used to determine the elemental composition of the particles. Nanoparticles samples were placed into a 42mm powder cup and covered with a 5 $\mu$ m thick polypropylene foil. The sample was analyzed using a QuanX EC benchtop EDXRF analyzer.

Scanning electron microscopy (SEM) using FEI Quanta 600 FE-SEM was used to determine the particles surface structure and size. Elemental analysis was also performed using the SEM accessory Oxford INCA EDS equipped with X-ray mapping and digital imaging. This allowed for elemental analysis of elements that lie below aluminum in the periodic table, one of the limitations with XRF. X-ray diffraction (XRD) was used to determine the likely surface structure of the nanoparticle surface.

XRD analysis was performed on a Bruker D8 powder diffractometer with Bragg-Brentano Geometry and having a LynxEYE detector. The following conditions were used for data collection:  $\text{CuK}\alpha = 1.5418$ ; 40 kV, 40mA;  $2\theta$  start =  $10^\circ$ ,  $2\theta$  end =  $80^\circ$ , step size = 0.015, time per step = 0.1s.

## CHAPTER III

## RESULTS AND DISCUSSIONS

## A. Mercury Removal from Aqueous Samples Using Commercial Nanoparticles

Five metal oxide based nanoparticles, copper oxide (CuO), titanium dioxide (TiO<sub>2</sub>), aluminum dioxide (Al<sub>2</sub>O<sub>3</sub>), silicon dioxide (SiO<sub>2</sub>) and iron (III) oxide (Fe<sub>2</sub>O<sub>3</sub>) were evaluated for their ability to remove mercury from solution at a concentration of 2g/L. As Hg(II) is the most stable form found in a typical aqueous systems, we have focused on the removal of this species as compared to the other reduced forms [53]. Besides running the experiments without adjusting the pH we have also used buffered systems to ensure that the pH is in the natural range between pH 6.5 and pH 8.5. Table I details the results of our evaluation. Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> commercial nanoparticles demonstrated the greatest removal efficiencies (above 83% removal for both the buffered and non-buffered systems. Silica nanoparticles demonstrated the worst observed removal during the evaluation period. Aluminum oxide demonstrated approximately 80% removal of mercury in the non-buffered system, but we observed a 40% reduction in removal of mercury in the buffered system. The copper oxide nanoparticles resulted in 65% removal of mercury from non-buffered condition and 80% removal in the buffered solution.

In the table below,  $C_f$  represents the concentration of mercury in the reactors. The initial concentration was 100 ppb (nominal) of mercury. The actual initial mercury concentration was used to determine the mean % removal.



Table I. Mercury removal by five commercially available metal oxides and an industrial resin

Metal Oxide	Mean Conc(stdev) in ppb		Mean % removal		pH	
	$C_f$ Unbuffered	$C_f$ Buffered	Unbuffered	Buffered	Unbuffered	Buffered
TiO <sub>2</sub>	0.21(0.18)	15(0.9)	> 99	83	5.44	8.87
Fe <sub>2</sub> O <sub>3</sub>	8.65(1.8)	11.3(3.3)	89	87	4.21	8.61
Al <sub>2</sub> O <sub>3</sub>	16.97 (1.8)	46.2(20.4)	78	46	4.71	8.92
CuO	28.43(3.1)	17.1(0)	63	80	5.07	8.84
SiO <sub>2</sub>	No removal	82.7(4.8)	Minimal	Minimal	9.64	9
Resin	44.1(26.5)	36(9.6)	45	58	3.91	8.7

## B. Surface Amended Nanoparticles for Increased Mercury Removal

Previously published literature and experimentation with the five commercial nanoparticle informed our decision of which nanometal oxide to select for surface modification. Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> were not considered candidates for surface modification, because these two commercial nanoparticles demonstrated the highest mercury removal of the five evaluated particles. Silicon dioxide was immediately ruled out due to its poor performance. In addition, Brown et al. [43] had previously created thiol-functionalized nanoporous silica that were efficient at reducing levels of Hg<sup>2+</sup> in aqueous solutions to below 10 ppb. Aluminum oxide was not further investigated because 80% mercury removal was observed for non-buffered water, but there was a 40% reduction in mercury removal in the buffered system. Pacheco et al. also had previously synthesized different concentrations of alumina sol and reported 94 – 100% removal depending on the amount of sol used [45]. Copper oxide nanoparticles showed similar mercury removal as the aluminum oxides with 65% removal from non-buffered systems and 80% removal under buffered conditions. Surface modification of nanoparticles for mercury removal was not previously reported in the literature to the best of our knowledge. Therefore, copper oxide nanoparticles were the metal oxide particles selected for surface modification. Several authors have reported that surface bound sulfur containing groups, including sulfides [42],[54] and thiols [55],[43],[56],[20],[57],[58], increased mer-

cury affinity for surface complexation across particle sizes. Therefore, our research focused on modifying the surface of copper oxide nanoparticles with sulfur containing groups. Use of alkanethiol as a surface modification agent was reported to create both thiol functionalized surfaces, as well as sulfide functionalized surfaces. Starting with the limited available literature for surface modification with alkanethiols, the method reported by Zhu et al. (refer to methods section Creating Novel Surface Amended Copper Oxide Nanoparticles for method details) was followed to produce a black nanoparticle powder. 1-octanethiol was then coated onto the resulting black nanoparticle powder and the black particles that resulted after the addition and vacuum evaporation of 1-octanethiol were examined using XRF, XRD, and SEM to determine the resulting surface structure. XRF analysis of these particles gave the elemental composition of these particles to be copper and sulfur (Figure 1).

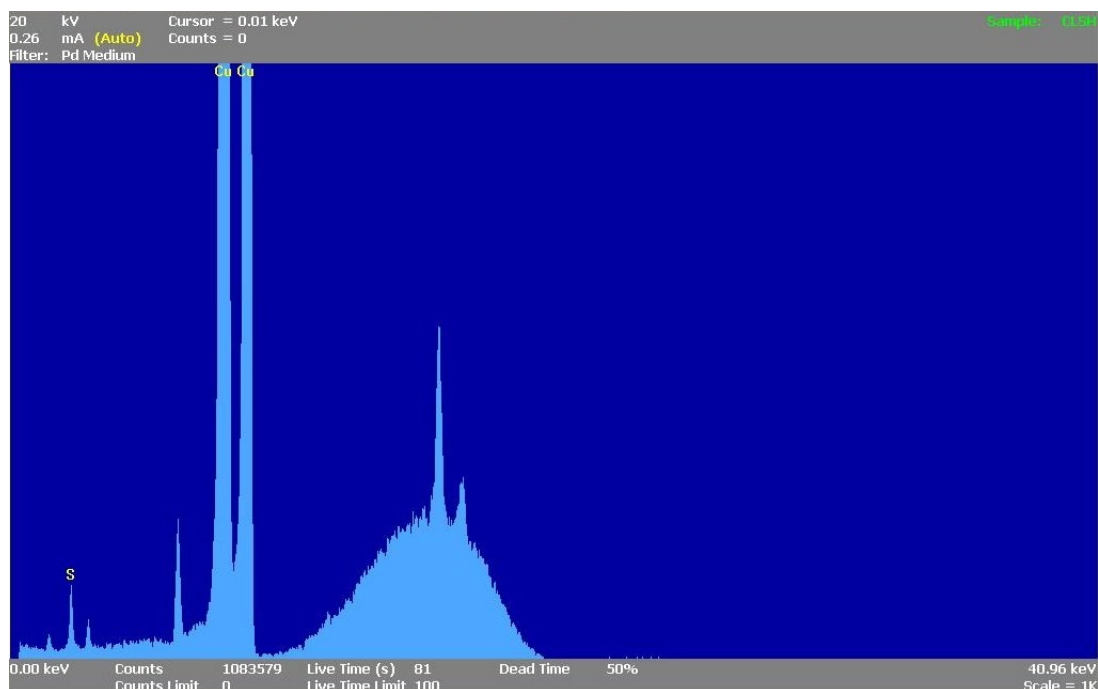


Fig. 1. XRF analysis of laboratory prepared thiol treated CuO nanoparticles

XRD was then used to evaluate the surface structure of the laboratory prepared nanoparticles. Figure 2 shows the XRD spectra for our laboratory prepared nanoparticles. The primary peaks of copper identified were CuO. We also determined the presence of severe contamination with sodium acetate ( $\text{CH}_3\text{COONa}$ ). CuO peaks are indicated with the red bars and the multiple sodium acetate peaks are indicated in blue in Figure 2. The pattern in black color indicates XRD spectra for laboratory prepared CuO while the red pattern indicates spectra for the same particles but coated with thiol. The XRD library did not confirm the presence of copper-sulfur containing

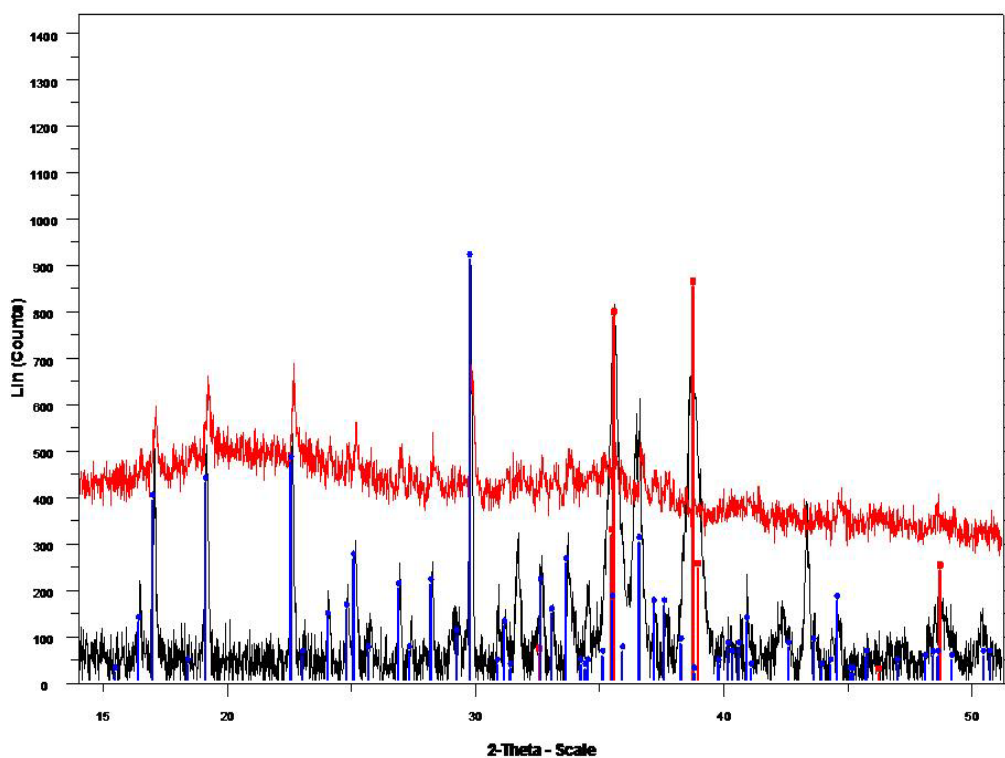


Fig. 2. XRD analysis of the laboratory prepared thiol treated CuO nanoparticles groups on the surface. Because the high amount of sodium acetate impurity created a

very messy spectrum, we decided to rinse the prepared particles again with water and ethanol. Once the additional rinsing steps were complete, we again ran the XRF and XRD analysis. The XRF analysis (Figure 3) on the rinsed particles showed a reduced sulfur signal on the surface compared to the particles that were not rinsed following addition of 1-octanethiol. XRD analysis (Figure 4) of the rinsed particles gave a

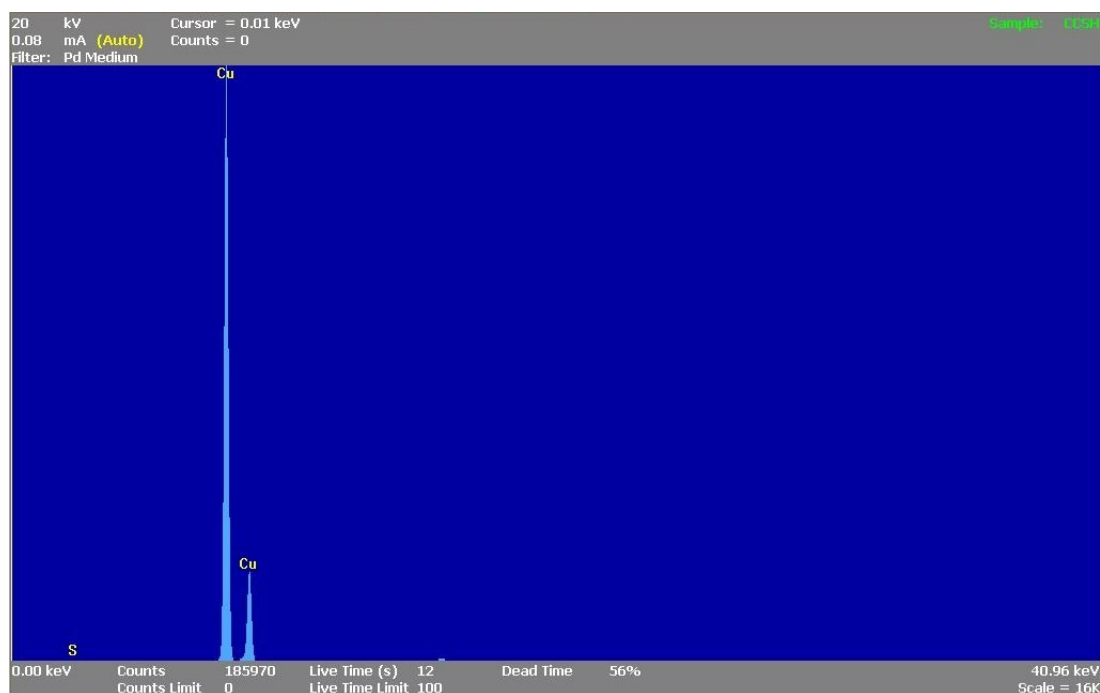


Fig. 3. XRF analysis of laboratory prepared CuO rinsed particles treated with thiol surprising result: the particles were now copper nanoparticles (blue bars in Figure 4) instead of the expected copper oxide nanoparticles. Ethanol reduced the copper oxide to copper and sodium acetate hydrate was still a major surface impurities (red bars in Figure 4). Because of the presence of high levels of impurity and the lack of a confirmed copper-sulfur complex we decided to depart from the Zhu et al. method and to develop a new method for creating surface amended copper nanoparticles.

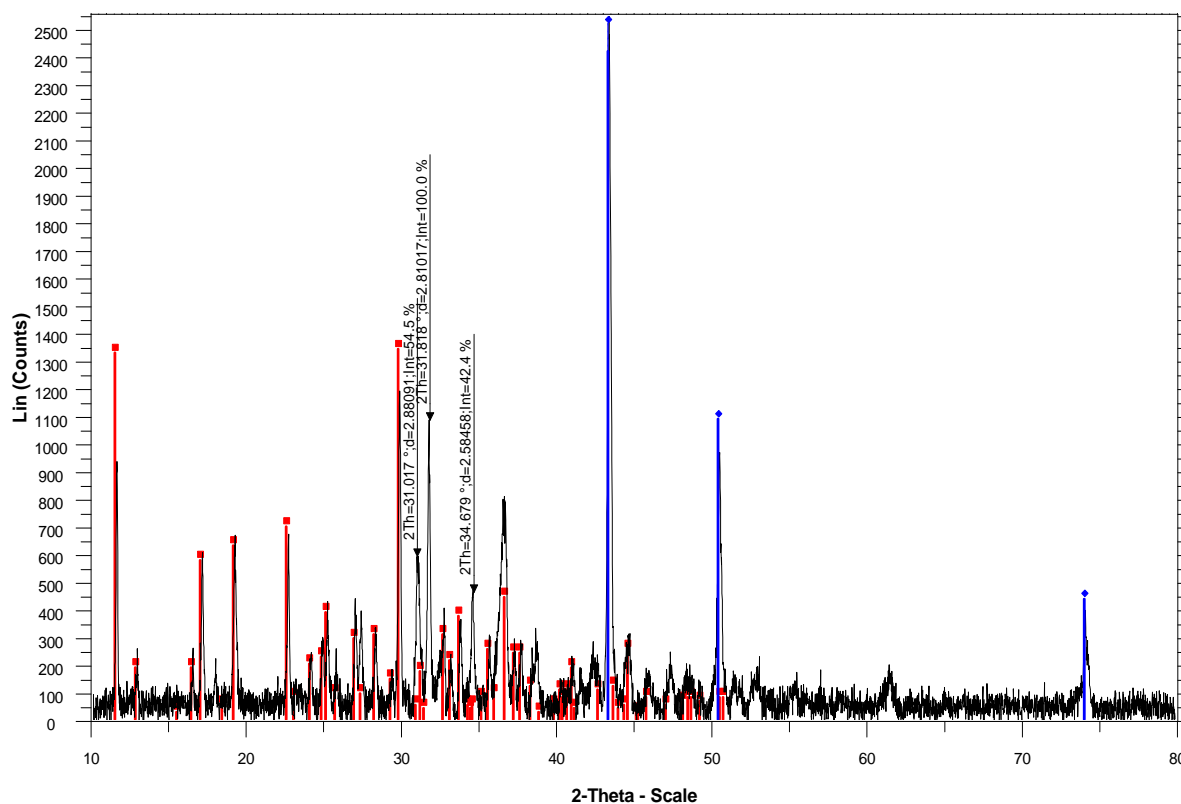


Fig. 4. XRD analysis of rinsed copper (oxide) nanoparticles

In order to limit the number of reaction components that could potentially interfere with successfully making sulfur amended copper nanoparticles, we limited the amendment reaction to only coating commercial copper oxide nanoparticles with 1-octanethiol. This simple, but efficient method, produced a XRF spectra (Figure 5) that confirmed the presence of copper, as well as sulfur. XRD analysis (Figure 6) showed that when the commercial copper oxide was coated with thiol the apparent resulting surface structure was a mixture of copper sulfides -  $\text{Cu}_2\text{S}$  (chalcocite, blue bars) and  $\text{Cu}_{1.8}\text{S}$  (digenite, red bars).

Discussions with the XRD technician could not rule out the presence of thiol functionalized surface groups, as the library did not contain copper thiol minerals

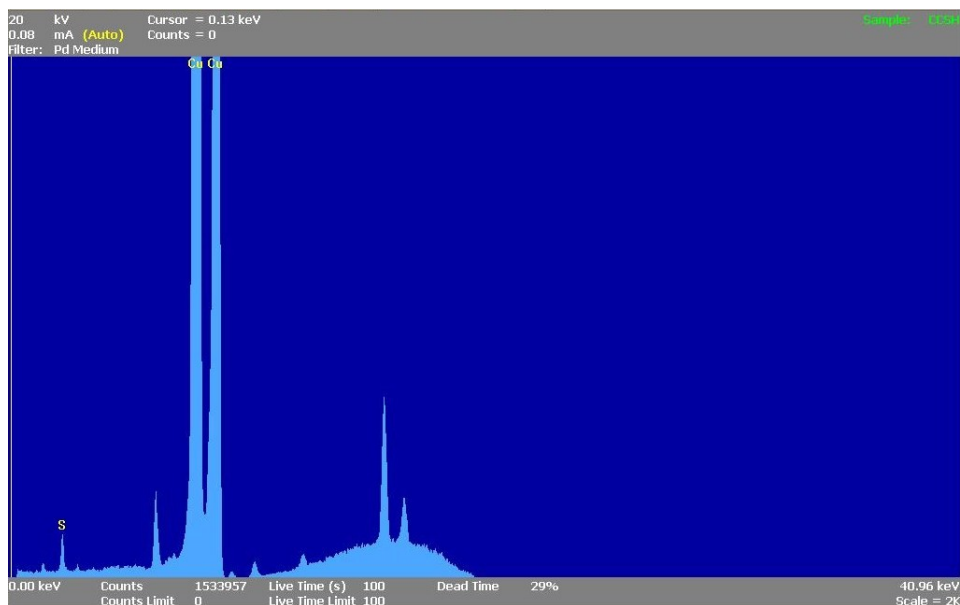


Fig. 5. XRF analysis of commercial CuO treated with octanethiol

because they are rare. SEM was used to provide a second opinion on the surfaces elemental composition as well particle size.

EDS analysis using a SEM (Figure 7) confirmed the presence of carbon on the surface, perhaps signifying that there potentially were alkanethiol functional groups on the surface.

However, the support for SEM is graphite, which may have also contaminated our particle surface with carbon. In addition, further review of available literature revealed two references that listed XRD spectrum for thiolated copper particles [59],[60]. The XRD spectra in the literature were markedly different from the XRD spectra of our sulfur containing copper nanoparticles. Therefore, it has been reconfirmed that our nanoparticles were a mixture of the two copper sulfides.

SEM images depicting the difference between the original commercial copper oxide nanoparticle and our coated particles are presented in Figures 9 and ??.

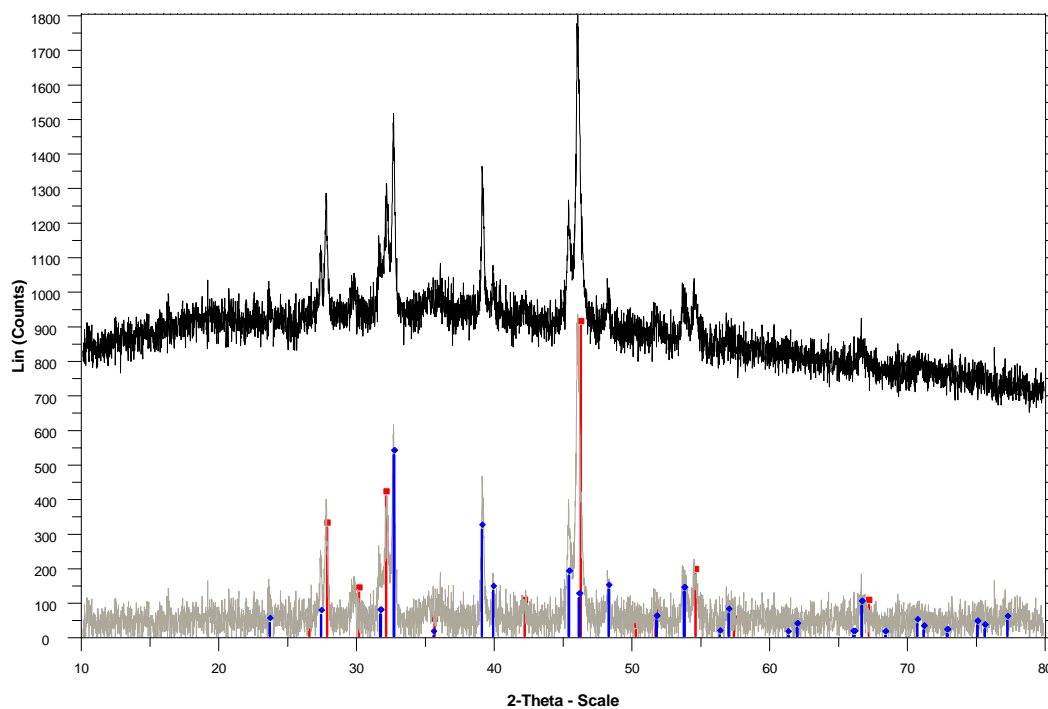


Fig. 6. XRD analysis of commercial CuO treated with octanethiol

Both images show that the nanoparticles tend to coalesce together. While it was difficult to measure the size of the individual nanoparticles, the coalesced particles were on the order of several microns. The elemental composition of the two particle types were also different, with the commercial copper oxide nanoparticles only containing copper oxide.

### C. Mercury Removal with Novel CuS Nanoparticles

The mercury removal experiments were conducted using the newly coated nanoparticles. The surface amendment increased the removal of mercury in our laboratory prepared buffered and non-buffered aqueous solution to above 99% in both conditions. This performance surpasses the performance of the five evaluated commercial

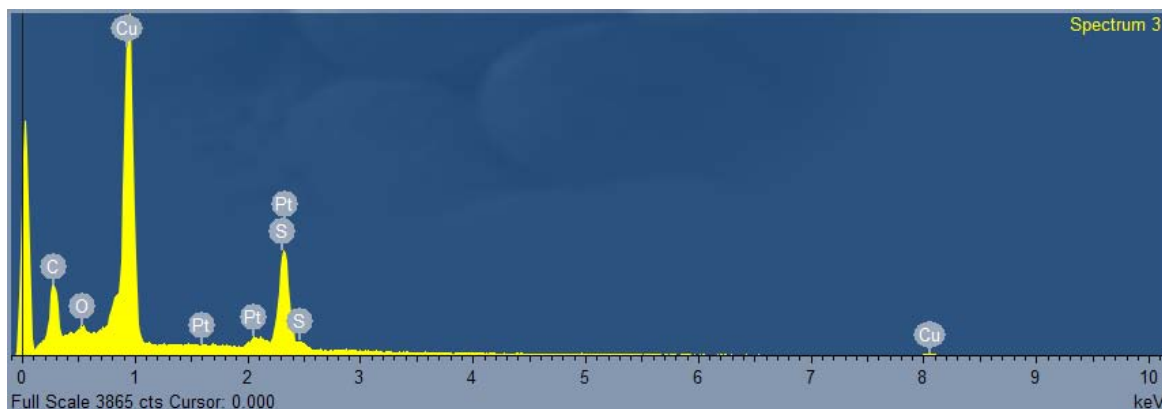


Fig. 7. EDS analysis using SEM for commercial CuO treated with octanethiol nanoparticles, thereby meeting the goal of our research project. Only one other group has published on mercury removal using CuS nanoparticles [54]. This group concluded that CuS can reduce the  $\text{Hg}^{2+}$  concentration from an initial concentration of  $20\text{ppm} \pm 2\text{ppm}$  to a final concentration of  $14\text{ppm} \pm 2\text{ppm}$ . However, their particles were never completely characterized to determine their actual structural composition. Nevertheless, their results do corroborate the high affinity for mercury removal of copper sulfide-containing nanoparticles.



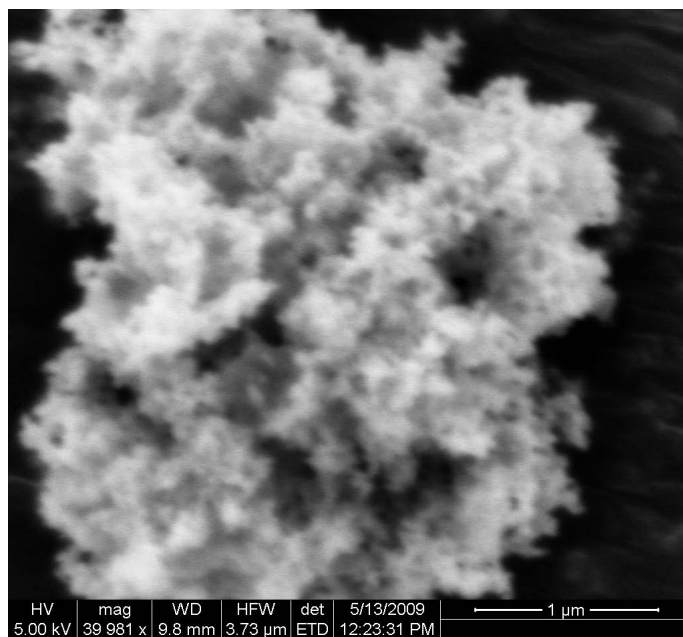


Fig. 8. SEM analysis of commercial CuO nanoparticle without thiol

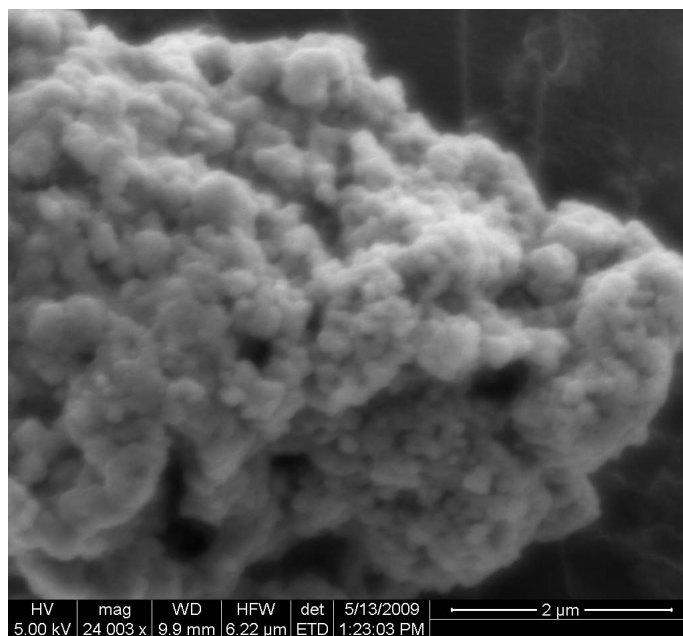


Fig. 9. SEM analysis of commercial CuO nanoparticle with thiol

## CHAPTER IV

### SUMMARY

#### A. Conclusion

The major conclusions realized from this study were:

- Five commercial metal oxide nanoparticles and a commercial resin were evaluated for their ability to remove mercury from a buffered and non-buffered aqueous solution. Titanium dioxide and iron oxide gave the best mercury removal ( $> 83\%$ ) while oxide of silica demonstrated the least removal efficiency. Copper oxide demonstrated  $65\%$  removal of mercury from non-buffered condition and  $80\%$  removal in the buffered solution whereas aluminum oxide resulted in  $78\%$  removal of mercury from non-buffered condition and  $46\%$  removal in the buffered solution. The commercial resin also performed poorly
- XRF, XRD and SEM analyses were used to characterize the surface structure of the novel particles that were created based upon coating commercial nanoparticles with 1-octanethiol. They were found to be a mixture of two copper sulfides namely  $\text{Cu}_2\text{S}$  (chalcocite) and  $\text{Cu}_{1.8}\text{S}$  (digenite)
- Surface amended nanoparticles achieved  $> 99\%$  mercury removal for both the buffered and non-buffered aqueous systems used in our experimental system

#### B. Future Scope

There is a much potential in these nanoparticles to remove mercury from aqueous solutions. However, the impact of different system conditions (such as temperature, organic carbon, and other metals) needs to be further characterized. Additional

analytical techniques such as nitrogen adsorption (isotherm), X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR) will help us to understand the structure better. Kinetic experiments also need to be conducted in order to understand the rate of mercury removal by the nanoparticles. Finally, desorption studies will need to be assessed before kinetic models can be developed to predict adsorption and desorption of mercury from the nanoparticle surface. Each of these remaining issues should be addressed as part of future work.

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