ADSORPTION, PHOTOCATALYSIS, AND PHOTOCHEMISTRY OF TRACE LEVEL AQUEOUS MERCURY

By

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To my father
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Mercury (Hg) is ubiquitous in the environment and can lead to detrimental impacts for humans and ecosystems. From the literature, semiconductor photocatalysis showed promise as an aqueous Hg removal technology. To further this concept, high surface area photocatalytic adsorbents, SiO\textsubscript{2}/TiO\textsubscript{2} composites (STC), were synthesized by adding TiO\textsubscript{2} nanoparticles to a liquid sol that was catalyzed by HNO\textsubscript{3} and HF acids. The resulting materials were characterized by SEM, nitrogen adsorption-desorption, streaming potential, XRD, diffuse reflectance and TiO\textsubscript{2} surface area analyses. Approximate characteristics include an isoelectric point of 3, TiO\textsubscript{2} particle size of 30 nm, and a band gap energy of 3.2 eV. Surface areas of the composites ranged from 167 to 630 m\textsuperscript{2}/g. Available TiO\textsubscript{2} surface area of the composite was dependent upon TiO\textsubscript{2} loading.

STCs and their precursors, silica and Degussa P25 TiO\textsubscript{2}, were applied to trace level Hg solutions (100 µg/L Hg) to determine the degree of Hg removal that could be accomplished via adsorption and photocatalysis. Under adsorption alone, STCs were able to achieve approximately 90 % Hg removal. Silica without TiO\textsubscript{2} performed poorly and was not affected by UV illumination. Additionally, Hg removal was optimized by altering primary particle size, STC pore size, and TiO\textsubscript{2} loading. Contrary to expectations, the performance of DP25 was not
significantly improved by UV irradiation and the performance of the STC was degraded under the same conditions. Elemental Hg was formed under UV irradiation due to photochemical reactions, decreasing the Hg removal by STC.

Photochemical transformations of Hg in batch reactors were investigated. The effect of purge gas (including rate and bubble size), UV irradiation wavelength, initial Hg concentration and time on Hg removal from prepared solutions were studied. Nitrogen purge with 254 nm UV irradiation resulted in the greatest net production of elemental Hg following a pseudo first order rate constant of 0.18 s\(^{-1}\) reaching over 99% removal. As oxygen was introduced into solution, the quantity of elemental Hg volatilized decreased but still resulted in significant Hg losses through volatilization up to 90% in 60 minutes. Most importantly, the loss of elemental Hg from solution is dependent upon the gas purge rate and bubble size.
CHAPTER 1
INTRODUCTION

In the late 1950’s, the Minamata tragedy alerted the world to the danger of mercury (Hg) pollution to human health. From 1932 to 1968 copious amounts of Hg were spilled into the Minamata Bay in Japan from an industrial process which used Hg to catalyze a reaction to produce acetaldehyde resulting in severe contamination of the bay. The fish population, that was a food staple for people in the region, became highly contaminated with methylmercury (MeHg). Subsequently, the consumption of these fish resulted in a neurological syndrome in adults (often called the Minamata Disease) and mental retardation, seizures, and cerebral palsy in fetuses exposed to MeHg during gestation leading to the loss of over 100 lives and permanent damage to many others.\(^1\)\(^2\) This tragedy was the first insight into the toxic nature of Hg. Hg pollution can also cause detrimental impacts to the health of the flora and fauna in an ecosystem.

Many industrial activities, past and present, contribute to Hg pollution. Hg-laden wastewater may be generated by sources such as dental offices, hospitals, laboratories, coal-fired power plants employing wet scrubbers, and chlor-alkali facilities employing an Hg-cell process. The current discharge level in the northern U.S. by the Great Lakes Initiative Wildlife Criteria is 1.3 ng/L.\(^3\) If this standard is extended throughout the country, Hg emissions from a variety of sources would need to be greatly diminished. Additionally, governments around the world have adopted seafood consumption advisories and recommended safety levels of fish consumption to protect the populations from Hg poisoning.\(^4\) Therefore, it is clear that to meet advisory levels and protect human health and the environment, Hg pollution needs to be controlled.

Hg pollution of natural systems continues to be an issue of concern on a global scale especially with respect to the contamination of food supplies.\(^5\) This concern is primarily due to the ability of MeHg compounds to bioaccumulate/biomagnify in the food chain and to negatively
impact living organisms. In the US, a large percentage of the population remains exposed to Hg levels that are well above government’s established health advisories. To protect the population, the US-EPA requires that potable water must meet a maximum contaminant level of 2 µg Hg/L and recommends the implementation of fish tissue-based water quality criterion to meet the Clean Water Act requirements. To meet fish tissue-based water quality criterion, safe water column concentrations have to be established. These values will vary based on location which dictates the tendency for MeHg production and accumulation, but most likely would require sub-µg/L levels. These levels call for the development of new remediation techniques that can treat trace level aqueous Hg waters to even lower concentrations.

Traditional technologies for Hg removal, such as precipitation, have struggled to reach such low ng/L concentrations that are desired for a healthy environment and population. A robust technology that can treat waters of various characteristics, can be regenerated, and can lower Hg concentrations to 1.3 ng/L is desired. However, the removal of Hg at µg/L or ng/L levels, such as is necessary for regulations to protect human health, is not well explored. In response, Hg phenomena at low concentrations need to be investigated. In addition to filling a gap in the literature, low level Hg removal technologies will enable industries to reduce pollution, resulting in extreme benefits to human and wildlife health and the environment.

This work focuses on understanding the physical and chemical properties of high surface area photocatalytic adsorbents, SiO₂/TiO₂ composites (STC). Silica-titania composites have been used for many applications in semiconductor photocatalysis. While titania particles act as a photocatalytic center, silica gel provides a semi-transparent macrosupport for the nanosized titania, enabling tailororable particle size for reduced filtering requirements, and increased surface area (>200 m²/g) for greater adsorption capacity. The STC technology can be adapted for
various treatment stream applications such as in line, batch, or pump and treat configurations. Specifically, it has been successfully applied for Hg removal from flue gas\textsuperscript{14,15}, Hg recovery from caustic exhaust emitted from the chlor-alkali industry\textsuperscript{16}, and the degradation of volatile organic compounds in gas emitted from pulp and paper mills.\textsuperscript{17}

With this understanding, the material could be applied and optimized for aqueous Hg removal in attempts to identify a technology to achieve the goals stated earlier. As steps to reach a rigorous trace level aqueous Hg removal technology the following hypotheses and goals were identified.

Hypotheses:

1. As semiconductor photocatalysis has been found to be a promising Hg removal technology via TiO\textsubscript{2}, the application of silica-titania composites using DP25 (a commercially available TiO\textsubscript{2}) would further enhance Hg removal capabilities due to a higher specific surface area while also decreasing energy requirements for solid separation facilitated by a tailorable primary particle size.

2. The addition of a DP25 would not impact the composite structure and the quantities added would have a direct correlation to available TiO\textsubscript{2}.

3. Photocatalytic reduction of Hg would occur through the activation of TiO\textsubscript{2} valence band electrons and result in the production of elemental Hg which can sorb to TiO\textsubscript{2} in higher quantities than divalent aqueous Hg.

4. The presence of UV would influence Hg chemistry.

5. The presence of organic compounds in solution would increase Hg reduction and removal by scavenging photogenerated h\textsuperscript{+} and would beneficially lower both Hg and TOC concentrations.

6. The presence of oxygen in solution would contribute to the formation of less Hg\textsuperscript{0} from the Hg\textsuperscript{2+} ion.

Objectives:

1. Synthesize STC with various properties (i.e., pore size and TiO\textsubscript{2} loading) suitable for Hg removal.

2. Characterize STC with various techniques (i.e., SEM, nitrogen adsorption-desorption, streaming potential, XRD, diffuse reflectance, and TiO\textsubscript{2} surface area analyses ).
3. Assess the performance of STC for Hg removal by comparing photocatalysis and adsorption mechanisms.

4. Identify the optimal STC formulation (e.g., pore size distribution, surface chemistry, titania loading) or optimization technique for Hg removal.

5. Screen the technology for treatment of natural effluents.

6. Further explore the impact of UV light on the aqueous speciation of Hg.
Mercury

Hg has become a targeted pollutant due to its toxic nature which is intensified through bioaccumulation in plants, fish, and wildlife. Hg has always been present in the environment due to natural sources since it is found in all geological materials to some degree. However, when industrial and governmental uses of Hg concentrate the chemical in the surrounding area and the atmosphere, it becomes an issue of concern. Hg is a heavy metal that cannot be created or destroyed, so it partitions between air, water, and sediments in the environment.

Sources

An estimated 4,400 to 7,500 tons of Hg are released into the environment worldwide each year. These releases are composed of natural and anthropogenic sources. Natural releases of Hg emerge from their original deposits through occurrences such as volcanic activity and fires. On the other hand, many industrial activities, past and present, contribute to anthropogenic Hg pollution. Throughout the world, gold mining, pharmaceutical industries, chlor-alkali chlorine manufacturing processes, batteries, thermometers and light bulb production, metal processing, power production, etc. contribute to Hg releases to solid, liquid and gaseous media.

A significant portion of global Hg emissions stems from the coal fired power industry. Hg is a naturally occurring element found in coal. When the coal is burned for the production of power, Hg is released as an air pollutant. In the United States of America (US), the Environmental Protection Agency (EPA) has recently begun focusing on placing limits for Hg air releases from this industry. This will require implementation of pollution control devices. These treatment systems are likely to include co-controls such as flue gas desulfurization (FGD) scrubbers or activated carbon injection. There is potential in the FGD process to capture
oxidized Hg in the scrubber water and create a liquid waste stream. This would lead to
cumulation and possible high concentrations of Hg in the scrubber water. Currently
unrecognized as hazardous, this waste stream may require aqueous Hg removal in the future.
Both control options will likely accumulate Hg on the solid substrates (calcium complexes and
carbon) which may then cause a leachate problem due to construction applications or landfilling
of the FGD byproducts. The transport mechanisms involved are currently being studied.\textsuperscript{19,22}

In recent years, the significance of Hg emissions from the chlor-alkali industry,
employing Hg cell technologies, has come into light.\textsuperscript{23} In this process, chlorine is produced in
electrolysis cells where a brine solution and Hg flow concurrently as an electrolyzer. Hydrogen
gas and alkali metal hydroxide are formed as byproducts. The release of Hg-laden waste streams
(liquid and gas) into the environment is the largest issue of concern associated with this
separation process.

Other smaller sources of Hg emissions constitute the remainder of the anthropogenic
releases. The culmination of all of these sources leads to widespread and persistent pollution
which can exhibit a range of health impacts on ecosystem, wildlife and human health.

\textbf{Health Impacts}

\textbf{Primary exposure}

Generally, Hg species can be classified as inorganic or organic. While inorganic Hg,
which exists as the metallic form, or in a variety of complexes with other inorganic elements, has
associated health hazards, methylmercury (MeHg), a commonly found organic Hg compound, is
considered to be more toxic. In water bodies, various forms of Hg are converted to MeHg by
microorganisms selective for Hg.\textsuperscript{24} When ingested, MeHg binds to proteins and amino acids and
accumulates in the food chain. The degree of Hg contamination a biological species exhibits is
dependent upon the life span, the quantity and type of consumption (trophic level), and Hg levels in the habitat. Because of all of these factors, MeHg concentrations can reach harmful levels.

Humans are primarily exposed to MeHg through the consumption of fish and shellfish. While fish are a good source of omega-3 fatty acids and are a lean protein source, both of which are beneficial to good health, consuming fish with high MeHg levels or other pollutants can lead to adverse health effects as shown by several studies. As MeHg is lipid soluble, it absorbs into the human gastrointestinal tract and penetrates cell membranes such as the blood-brain and the placenta. Because of this, Hg is most toxic to the brain and developing nervous system such as those in fetuses and young children. On average, fetal exposure to MeHg will be 70% higher than levels found in maternal blood exacerbating the impacts. In the U.S. approximately 5% to 10% of women of child-bearing age are estimated to exceed federal exposure guidelines due to dietary intake of Hg-contaminated fish. Based on a history of control groups exposed to Hg through environmental sources, hazardous levels and effects have been quantified.

History

The first insight into the toxic nature of Hg was revealed by a nationally known tragedy. From 1932 to 1968 copious amounts of MeHg were spilled into the Minamata Bay in Japan resulting in severe contamination of the water body. The fish population, that was a food staple for people in the region, became highly contaminated with MeHg. Subsequently, the consumption of these fish resulted in a neurological syndrome in adults (often called the Minamata Disease) and mental retardation, seizures, and cerebral palsy in fetuses exposed to MeHg during gestation.

On a less tragic scale, low-dose exposure has also been well studied in three epidemiologic longitudinal developmental studies: the Seychelles Child Development Study (SCDS); the child study in New Zealand; and the Faroe Islands child study which is still ongoing. The children
studied were maternally exposed to Hg through consumption of seafood with Hg contamination of varying levels. While the Seychelles study showed impairment occurring in some cognitive tests while not in others, prenatal MeHg exposure directly correlated to reduction in all tested cognitive responses for both the New Zealand and Faroe Islands studies.27-30

While developing populations are most susceptible, adult populations are still at risk. Excessive MeHg exposure has been linked to cardiovascular disease, paresthesia, ataxia, blurred vision/blindness, tremors, hearing impairment/deafness, slurred speech and difficulty walking. High dose exposure leads to even more severe neurodevelopment defects and death while low dose exposure results in subtle neurological dysfunction that manifests itself as learning disabilities.6

Impacts

Through the established long term studies discussed above, dose response functions (DRF) can be established to correlate Hg exposure to quantitative measures such as loss of intelligent quotient (IQ). A linear correlation was found to exist between IQ loss and Hg concentration in the cord blood of newborn children above a concentration of only 5.8 µg/L.31 Linear DRF have since been established and widely used ranging from 0.13 to 0.465 IQ decrement for each part per million of Hg in hair. This loss of IQ leads to an economic disadvantage being placed on the individual, greater loss of economic productivity, increased need for special education and healthcare and other costs. While estimates of the dollar values of these costs widely vary, the estimates range from hundreds of millions to billions of dollars per year.32,33 Without regulation, the American public suffers the burden of these costs.

Therefore, Hg is well established as a neurotoxin which can be problematic at extremely low concentrations and public exposure should be limited. Women who may become pregnant, women who are pregnant, breastfeeding mothers and young children are most susceptible to
these adverse health issues from MeHg exposure. As the human body will slowly clear MeHg at about 1% per day (which is equivalent to a half life of about 70 days) recovery from MeHg exposure can be long realized.\textsuperscript{34} A balance between eating a healthy diet including the benefits from fish while minimizing harmful exposure to MeHg needs to be achieved.

**Regulation**

Most government regulations and public health decisions are based on risk assessments. For Hg, the majority of risk assessments are based on protecting the health of the fetal nervous system from MeHg. In the US, non-carcinogenic chemicals use the exposure reference dose (RfD) as a quantitative health risk assessment factor. Using a benchmark dose lower limit (BMDL) of 58 ppb (equivalent to Hg levels in maternal blood), the RfD for Hg equals 1.081 \( \mu g \) Hg/kg body weight/day.\textsuperscript{35} To alert populations to the concerns of Hg concentrations in fish and the consumption of this food source, fish advisories are issued by government bodies or nongovernmental organizations (NGOs). In general, the advisories are very specific and pertain to a certain chemical, water body, species of fish, and/or group of people. The goal of the advisory is to have sensitive populations be aware of the issue and consume smaller quantities of the fish in question while not discouraging the consumption of fish for an important part of a well balanced diet.

With the copious number of fish advisories, and the consumption of fish being the main exposure route of humans to Hg hazards, a reduction in fish tissue Hg concentration is necessary to protect the ecosystem and human health. The first obvious conclusion is that water concentrations of Hg need to be reduced in order for fish populations to rebound. In the US, Hg is listed as a toxic pollutant under section 307(a) of the Clean Water Act (CWA). Per this ruling, aqueous discharge Hg concentrations must meet technology based effluent limits specific to the industry producing the waste. Regulation of this requirement is accomplished through a
permitting system called the National Pollutant Discharge Elimination System (NPDES). Currently, over 8,000 water bodies exceed water quality standards for Hg and will require implementing total maximum daily loads (TMDLs).\textsuperscript{19} For the protection of human health, the EPA has recommended that TMDLs be based on achieving fish tissue concentrations of less than 0.3 mg MeHg/kg fish.\textsuperscript{10}

States do have the power to require lower effluent limits and/or additional monitoring requirements than those of the technology–based standards specified by the EPA.\textsuperscript{36} In the Great Lakes region, where water quality had become exceedingly polluted, auxiliary action was deemed necessary. Several movements were taken by both local and national governments. Water quality standard Hg criterions of 1.8 ng/L for the protection of human health and 1.3 ng/L for the protection of wildlife were adopted.\textsuperscript{3,37} All contributions of Hg, including deposition from the atmosphere, will be taken into account and management strategies will be developed to meet these limits.

While the risks posed to human health from consumption of fish containing MeHg are of the highest concern, other sources of Hg hazards are also regulated. The EPA requires that potable water must meet a maximum contaminant level of 2 µg Hg/L.\textsuperscript{8} This, in combination with TMDL development, requires extremely low levels of Hg being maintained and released into the environment.

**Chemistry**

Hg found in the environment can take many forms which impact its bioavailability and toxicity. The degree of bioaccumulation of Hg in the environment is heavily dependent upon its abundance, environment and chemical nature. Hg is a p-block element with three stable oxidation states, Hg\textsuperscript{0}, Hg\textsuperscript{+}, and Hg\textsuperscript{2+}. It is unique in the fact that it is continuously cycling between the biosphere, hydrosphere, and geosphere. From the atmosphere, Hg chiefly reaches
surface waters through wet precipitation or deposition on aerosols. Once in aqueous systems, chloride and sulfide largely influence the speciation of Hg. Speciation of chloride systems have been extensively studied; mercuric chloride (HgCl$_2$) is the predominating Hg-Cl species accompanied by small amounts of HgCl$^+$, HgCl$_3^-$, and HgCl$_4^{2-}$ which is influenced by Cl concentration. As chloride concentrations reach $10^{-7}$ M, $10^{-4}$ M, and $10^{-1}$ M, the dominant species become HgCl$_2$, HgCl$_3^-$ and HgCl$_4^{2-}$ respectively.\(^{38}\)

In the presence of sulfur, black mercuric sulfide forms as a precipitate due to its extremely low solubility. In conjunction, other soluble forms of Hg can result such as HgS$_2^{2-}$ at high pH and Hg(SH)$_2$ at low pH. When present simultaneously, Hg-Cl species dominate in oxidizing and acidic environments, whereas Hg-S compounds are abundant in reductive systems.\(^{39}\) Therefore, in reference to natural surface waters, Hg-Cl complexes are found near the interface in oxygenated waters and sulfides are more dominant near the sediments in anoxic waters.\(^{24}\)

Fluoride, also commonly found in natural waters, will exhibit no significant effect on speciation. In aqueous systems, Hg and F remain completely dissociated.\(^{40}\)

Overall, hydration of Hg in aqueous solutions is also extremely relevant to speciation. Mercuric ions will hydrolyze to HgOH$^+$ and Hg(OH)$_2$ as in Equation 2-1 and 2-2, at a pH range from 2 to 6, above which generally all ions will be hydrated as Hg(OH)$_2$.\(^{38}\) Hg has not been found to hydrate to a greater extent than Hg(OH)$_2$.\(^{39}\)

$$\begin{align*}
Hg^{2+} + H_2O & \leftrightarrow Hg(OH)^+ + H^+, K = 2.6 \times 10^{-4} \\
HgOH^+ + H_2O & \leftrightarrow Hg(OH)_2 + 2H^+, K = 2.6 \times 10^{-3}
\end{align*}$$

Equations (2-1) and (2-2)

Further, a short discussion on Hg(NO$_3$)$_2$ is relevant to laboratory uses of Hg standards. Hg(NO$_3$)$_2$ ionizes in solution to form Hg$^{2+}$ and NO$_3^-$. The dominating speciation is simply ionic
or hydrolyzed Hg (Figure 2-1) in these systems in comparison to solutions prepared with chlorine or sulfur where more complexes are formed.41

![Figure 2-1. Predominant speciation of 100 μg/L (0.5 μM) Hg as prepared from Hg(NO₃)₂ calculated with Mineql+ under the given conditions](image)

Photochemistry

Hg chemistry and speciation have also been recognized to be affected by the presence of light. Photochemical reactions, therefore, will impact Hg bioavailability. Measured dissolved gaseous Hg (DGM) concentrations have been well correlated with the intensity of solar radiation in water bodies.42-46 Other studies have shown Hg volatilization from sun exposed solid matrices such as Hg-contaminated sewage sludge and soils.47,48 Therefore, it has become widely accepted that the absorption of photons leading to primary and/or secondary photoreactions is responsible for a significant portion of ionic Hg to Hg⁰ in the environment. However, compounds such as hydrogen peroxide, dissolved organic carbon and iron chemical species are believed to play a significant role in the photochemical reduction reactions.49-51

Understanding of the mechanisms leading to DGM production remains limited. Many attempts have been made to pinpoint the reactions leading to reduction of ionic Hg or oxidation
of Hg. The aim of a study by Amyot et al. was to determine the effect of hydrogen peroxide on production of DGM. Two equations were proposed (Equation 2-3 and Equation 2-4):

\[
\begin{align*}
Hg^0 + H_2O_2 + 2H^+ & \rightarrow 2H_2O + Hg^{2+} \\
H_2O_2 + 2OH^- + Hg^{2+} & \rightarrow O_2 + 2H_2O + Hg^0
\end{align*}
\tag{2-3}
\tag{2-4}
\]

It was found that at pH 5.5, DGM levels were significantly lower when spiked with hydrogen peroxide. Below pH 5.5 H_2O_2 acts as an oxidizer while above this pH, it is a reductant. In 1997, Amyot et al. found that Hg in saltwater samples indeed experienced photoinduced reduction. Rapid re-oxidation also occurred and was attributed to the chloride content of the water. Zhang and Lindberg suggest that photochemical reduction is mediated by the production of free radicals as a result of Fe(III)-organic acids photolysis (Equation 2-5). It is also mentioned that dissolved oxygen may catalyze the reduction through the production of superoxide free radicals (Equation 2-6). Further, additional hydroxide radicals could be generated by the direct photolysis of dissolved organic carbon (DOC)(Equation 2-7) and contribute to oxidation of Hg.

\[
\begin{align*}
H_2O_2 + Fe^{2+} & \rightarrow \cdot OH + OH^- + Fe^{3+} \\
\cdot O_2^- + Hg^{2+} & \rightarrow Hg^0 + O_2 \\
D\cdot OC + H_2O_2 + hv & \rightarrow \cdot OH + products
\end{align*}
\tag{2-5}
\tag{2-6}
\tag{2-7}
\]

Research by Lalonde et al. investigated photooxidation of Hg in natural and artificial water with concentrations of dissolved elemental Hg. Data supported the chloride ion as a stabilizing agent for Hg, therefore oxidation by semiquinone radicals (produced by p-benzoquinone and UV) would be feasible in a progression from Hg^0 to Hg^+ to Hg^{2+}. Photooxidation only occurred when both chloride and Hg were present. In natural waters addition of chloride ions doubled the photooxidation rate. The overall conclusion of this work was that photooxidation requires chloride ions, a photoreactive chemical and the presence of light. With readily available
amounts of elemental Hg in solution, dark oxidation does occur in the presence of halogens through simple complexation reactions.\textsuperscript{44,53,54} Because of the co-occurrence of oxidation and reduction reactions, the accumulation of DGM occurs when rates of Hg-reduction reactions exceed that of oxidation. Mechanisms underlying the production of DGM are therefore very complex and remain poorly understood on account of the numerous interactions that occur.

**Mercury Removal**

Pollution prevention has become recognized as a key step towards pollution reduction. Beginning from the start, the use of Hg can be significantly reduced or even completely eliminated. Hg has been eliminated from paints, pesticides, certain batteries, thermometers and other products in many countries. Huge success has been realized in reducing the use of Hg thermometers, collecting used thermometers and preventing their disposal and likely re-emission into the environment.\textsuperscript{19} However, once pollution prevention solutions have been expended, end of pipe solutions are the next available option for reducing Hg concentrations in effluents. Environmental regulations continue to demand lower discharge concentrations. This requires treatment options that can reach these levels in an economically feasible manner. Several options have been analyzed for Hg removal from aqueous solutions on pilot or full scales including precipitation, adsorption, bioremediation, and other.\textsuperscript{55}

**Precipitation**

Since 1985, the EPA under the Clean Water Act requires industry to meet Hg discharge concentrations suitable for the applicable best available technology (BAT). For the chlor-alkali industry employing Hg cell technologies, the BAT for this wastewater is a sulfur precipitation process. The process introduces sulfide to the effluent stream to produce insoluble mercuric
sulfide that is separated from the waste stream via clarification or filtration to achieve below 50 
µg/L concentrations of Hg as per the following reaction (Equation 2-8):

\[ \text{Hg}^0 + \text{Hg}^{2+} + \text{Hg}^{2+} + 2S^{2-} \rightarrow 2\text{Hg}^0 + 2\text{HgS}_{(s)} \]  

(2-8)

Dependent upon pH and sulfide concentrations, this or other reactions can occur to form 
different Hg-S compounds. Mercuric sulfide (HgS) is favored at low pH and low sulfide 
concentrations. Hence, to achieve sufficient removal, the water chemistry generally needs to be 
altered. Optimal pH is around 4. If an excess of sulfur is added to the process, larger quantities 
of soluble Hg-S complexes will be formed, decreasing the removal rates. Therefore, the process 
needs continual monitoring and may not reach low enough Hg concentrations for discharge. The 
speciation of Hg in the effluent is speculated to be dissolved Hg-S compounds and hydrated Hg.

**Adsorption media**

Various sorbents such as activated carbons, silica, organic materials, resins, other metals 
and more have been applied to Hg removal from liquids. Activated carbons are widely used in 
aqueous pollution treatment and have been specifically studied for their selectivity for Hg 
adsorption. Waste products such as fly ash, bark, organic sewage sludge and several others were 
used to produce activated carbon for Hg applications. In some instances, materials were 
tested in order to find a more cost effective alternative. Municipal Solid Waste fly ash achieved 
the largest Hg adsorption with a capacity up to 4200µg Hg per g of adsorbent. In addition to 
new synthesis procedures, the carbon was also doped with some form of catalyst. Sulfur doped 
carbons have shown high affinity towards Hg resulting in significantly greater removal capacity 
than the base activated carbon. Nam et al. stated that sulfur derivative functional adsorbents 
cannot be maximized with supports such as activated carbon because of an inadequate number of 
accessible hydroxyl groups on the supports and in the mesopores. To bypass this drawback, their
research focused on applying the sol-gel synthesis technique to make a doped adsorbent. With that process, structural properties such as pore size and surface area could be controlled. The result was a thiol functional organoceramic adsorbent called SOL-AD-IV. Thiol functional groups are composed of sulphydryl groups so have similar reactions to those of sulfur impregnated activated carbons.\textsuperscript{64} Another type of thiol functionalized material is Thiol-SAMMS which has a ceramic substrate and was developed by the Pacific Northwest National Laboratory (PNNL). Thiol-SAMMS was shown to have a selective and high affinity for Hg.\textsuperscript{65} While these adsorbents may have a strong affinity for Hg, a commercially available system to reduce Hg to below 12 ng/L is not available.

**Bioremediation**

Biological treatment of Hg effluents utilize microbial enzymes that convert Hg compounds into insoluble elemental Hg or mineral phases (such as mercury sulfide).\textsuperscript{19} A study by Wagner-Dobler et al. resulted in a decrease of Hg concentrations from over 2 mg/L down to about 30 µg/L from chlor-alkali wastewaters with a fixed bed aerobic bioreactor housing Hg resistant strains of *Pseudomonas*.\textsuperscript{66} Successful treatment with bioremediation will depend on the impact of several variables on biological reaction rates. In addition to the difficulty in the disposal of biomass loaded with Hg, this treatment method did not achieve low enough Hg concentrations to meet standards exhibited in the Great Lakes Region to protect the environment (1.3 ng/L) or human health (1.8 ng/L).\textsuperscript{3,37}

**Other**

While difficulties arose in selectively removing very small quantities of Hg from other technologies, its reduction to elemental Hg followed by air stripping as a removal strategy was investigated to treat groundwater from the Department of Energy Savannah River Site.\textsuperscript{67} With up to 25:1 molar ratios of Sn:Hg, 138 ppt Hg solutions were decreased in concentration by 94%.
However, this method added an undesired Sn contaminant to the solution and was only applicable to easily reducible species of Hg.

Further yet, combining adsorption and photochemical reactions has been tested with activated carbon and TiO₂. Zhang et al. found that combining the two materials and providing UV irradiation doubled the adsorption capacity of Hg (initial concentrations of 60 to 200 mg/L) from that of activated carbon alone. It was postulated that increased removal stemmed from the soft acid-soft base interaction where metallic Hg was a preferred soft acid over cationic Hg. Also, functional groups on the carbon surface could have contributed to the generation of additional hydroxyl radicals to participate in photocatalysis. Alternatively, applying these principles with silica supported TiO₂ as a Hg control technology will be addressed by this work.

**Photocatalysis**

Photocatalysis relies on electron-hole pairs, produced by a semiconductor, to proceed in redox reactions. Semiconductor materials lack a continuum of electronic states and therefore exhibit a region over which no energy levels are available. This void region is referred to as the band gap and has a quantifiable energy. When excited, an electron from the valence band jumps the band gap into the conduction band leaving behind a hole thus creating the electron-hole pair. For an electron to reach a level of excitation to reach the conduction band, the semiconductor must be exposed to ultraviolet or near-ultraviolet light with a wavelength that correlates to an energy (energy of the photons) equal to or greater than the band gap energy of that material.

Once generated, the electron-hole pairs can either recombine and release heat, get trapped by surface sites, or participate in redox reactions. Recombination can occur on the order of nanoseconds. Therefore, it is crucial that the desired reaction with the hole or electron occur immediately (i.e., the reactants be readily available at the surface of the TiO₂). Both oxidation
and reduction of species present in the surrounding fluid can occur simultaneously. One or the other reaction can be suppressed with a scavenger. When an electron scavenger is introduced, anodic reactions will proceed and the process is referred to as photocatalytic oxidation. However, if the opposite is applied and a hole scavenger is used then photocatalytic reduction will proceed. Electrons will participate in the reduction of compounds adsorbed to the TiO\textsubscript{2} surface. If there is a lack of available ions for reduction, oxygen can be reduced. Oxidation reactions will generally proceed by water and hydroxyl groups being oxidized by the hole to hydroxyl radicals. Other additional reactions can occur to form hydroxyl radicals as well. Exact oxidative pathways of organic constituents in the liquid have not been narrowed down to one mechanism. It is speculated that either the hole or hydroxyl radicals can participate in oxidation reactions.

In the selection of a semiconductor for photocatalysis, several conditions are necessary for a successful system. The material must be able to change valence state to allow the electron-hole pair, have a low enough band-gap energy for excitation to be plausible, and have catalytic properties. If these conditions are met, heterogeneous photocatalysis can proceed. In addition, it is beneficial if the material is nontoxic, resistive to photocorrosion, and inexpensive. Through many investigations, TiO\textsubscript{2} is the most widely used and successful semiconductor applied for environmental remediation. TiO\textsubscript{2} has many robust qualities such as suitable band gap energy for many applications, resistance to photocorrosion, low toxicity, relatively low cost, high quantum yield and superior performance when compared to anatase phase alone. Degussa P25 (DP25), a readily available commercial TiO\textsubscript{2}, has particle sizes of about 30 nm with a surface area of about 50 m\textsuperscript{2}/g. This brand consists of approximately 30% rutile and 70% anatase phase particles. The two crystalline structures differ in their octahedron formation and linkage,
causing variation in density and band structures.\textsuperscript{69} DP25 is often used as a benchmark due to its enhanced photochemical properties attributed to the mixed phases of TiO\textsubscript{2}. Hypotheses regarding the mechanism attribute the enhancement to a space charge region due to the difference in band gaps of anatase (3.2 eV) and rutile (3.0 eV) allowing a delay in e\textsuperscript{-}/h\textsuperscript{+} pair recombination.\textsuperscript{74,75} DP25 has been found to exhibit a point of zero charge at about pH 6.\textsuperscript{76}

**Inorganic Photocatalysis**

When photocatalysis is applied to liquids for the removal of toxic metals, photocatalytic reduction is desired. Metals are commonly present in one of their positive valences in water. Therefore, reduction via electrons generated by semiconductor photocatalysis can cause the transformation of the metals into a less hazardous valence and/or facilitate their removal from the aqueous stream.\textsuperscript{72} In these systems, the semiconductor is generally applied in a suspended slurry and illuminated by UV light. As an alternative to photocatalysis, metals removal is largely achieved by precipitation reactions. These types of treatment systems require large amounts of chemicals for reaction and result in large amounts of waste. In addition, the system has to be continuously monitored and controlled to achieve the correct speciation for precipitation to occur. Hence, photocatalytic treatment of metals is a promising remediation treatment.

Many metals are capable of being reduced via photocatalysis. Photoreduction of a metal ion is thermodynamically feasible if the standard reduction potential of that metal ion is greater than the energy associated with the conduction band-edge of the applied semiconductor.\textsuperscript{77} Of the same concept, the oxidation potential of a chemical must be less than the valence band of the semiconductor to be photo-oxidized. These potentials are dependent on the location of the band-gap of the semiconductor. Overall, the band-gap will remain the same magnitude but will vary with pH of the solution. Ward et al. developed the two following equations to represent the shift
of valence band (vb) (Equation 2-9) and conduction band (cb) (Equation 2-10) potentials for TiO₂ as a function of pH at a standard temperature of 25°C.⁷⁸

\[
E_{cb}(eV) = -0.05 - 0.059pH \quad (2-9)
\]

\[
E_{vb}(eV) = 3.25 - 0.059pH \quad (2-10)
\]

By determining the speciation of the metal constituents in the water to be treated, the potentials for reduction can be determined. If those potentials are greater than that of TiO₂ at the desired pH, then the reaction will be thermodynamically feasible. Once a metal ion has been reduced, it can be adsorbed and extracted from the system. Some metals can be recovered from the surface of TiO₂ and recycled. For example, Hg has shown good recovery from TiO₂ using hydrochloric acid (HCl) or an aqua regia solution.⁷²

Applying the above conditions to Hg photocatalytic reduction, a cathodic system is desired to promote the reduction of ionic or complexed Hg. Reduction of these species would occur through reactions with the photogenerated electrons to produce elemental Hg which would deposit onto the titania surface. Reduction potentials of some possible reduction pathways (as compared to the normal hydrogen electrode (NHE)) are given below in Equations 2-11 through 2-15.⁷⁹ Note that the reduction potentials are greater than the conduction band of the TiO₂ at all pHs. Therefore, these are all plausible reactions in a TiO₂ photocatalysis system.

\[
2Hg^{2+} + 2e^- \rightarrow 2Hg^{2+}, E^0 = 0.911 \text{ eV} \quad (2-11)
\]

\[
2Hg^{2+} + 2e^- \rightarrow 2Hg^{0}, E^0 = 0.796 \text{ eV} \quad (2-12)
\]

\[
Hg^{2+} + 2e^- \rightarrow Hg^{0}, E^0 = 0.854\text{V} \quad (2-13)
\]

\[
HgCl₂ + 2e^- \rightarrow Hg^{0} + 2Cl^-, E^0 = 0.41V \quad (2-14)
\]

\[
HgCl₂ + 2e^- \rightarrow Hg^{0} + 4Cl^-, E^0 = 0.46V \quad (2-15)
\]

Another method of deposition and therefore removal from the aqueous solution is adsorption to the TiO₂ in the form of HgO. Once Hg has been reduced, HgO has been speculated to occur in the presence of oxygen at high pH (pH 11) (Equation 2-16).⁷⁹

\[
Hg^{0} + O₂ \rightarrow HgO \quad (2-16)
\]
The overall efficiency of photocatalysis reactions is highly dependent on the interfacial electron transfer rate. The transfer rate is tied to the rate of recombination of the electron-hole pair. Thus, to improve the rate of photocatalytic reduction, a hole scavenger is advantageous. In addition, in the absence of a scavenger, holes will tend to oxidize water. This process proceeds slowly hindering the rate of reaction. Many organic compounds have been used in Hg photoreduction tests such as salicylic acid, formic acid, methanol and citric acid. Studies on photoreduction of Hg over TiO₂ agree that there is a direct correlation to the concentration of hole scavenger to Hg conversion. Wang et al. found the amount of Hg photoreduced reached a maximum with concentrations from 5 to 20 mM of formic acid. Other studies found success with citric acid as a scavenger due to complexes that could be formed that had a high affinity for TiO₂ and facilitated reduction (Equation 2-17).

\[ Hg^{2+} \cdot nCit^{3n^-} + (3n - 2)H^+ + (18n - 2) \cdot OH \rightarrow 6nCO₂ + (13n - 2)H₂O + Hg^0 \]  

An alternative method of reducing the electron-hole recombination rate is altering the semiconductor. In a study by Skubal and Meshkov, anatase TiO₂ was successfully modified with L-arginine. Similarly, Cristante et al. chemically modified TiO₂ with e-aminothiazole. The modifications replaced hydroxyl functional groups with carboxyl groups. Newly created carboxyl functional groups increased the distance between electrons and holes which accumulated electrons on the surface to facilitate multi-electron transfer. The first modified TiO₂ reached 99.98% removal of Hg (an initial concentration of 150 mg/L to below the detection limit of 30 µg/L) in 2 hours without methanol and only 30 minutes with methanol. The second was tested at pH values of 3, 7, and 9 and reached 46%, 65%, and 99% removal of 10 mg/L Hg solutions respectively.
Another factor that can hinder reduction reaction rates is the presence of oxygen. Dissolved oxygen competes with Hg for valence band electrons. Therefore, to promote Hg reduction it would be beneficial to remove the competition. Oxygen removal can be accomplished by purging with nitrogen. This method has proven to be effective for initial Hg concentrations of around 100 mg/L, resulting in increased photocatalytic reduction of Hg. However, some research found that inhibition of Hg transformation due to oxygen occurred only at acidic to neutral pH. The lower a species reduction potential, the more likely dissolved oxygen is to scavenge the electron. Therefore, especially in low pH systems where the conduction band energy is higher, nitrogen purging is a key factor to obtaining high Hg removal rates.

As discussed above, reduction of species will be dependent upon the difference in the reduction potential and the energy of the conduction band. The redox potential of TiO₂ will shift with changes in pH tending towards more cathodic potentials at higher pH. Metal ions, on the other hand, retain a constant reduction potential independent of pH. Hg possesses various reduction potentials which will change dependent on speciation. At low pH, the reduction of these Hg complexes over TiO₂ would be lower than that at high pH. This has been frequently noted in the literature. Chloride has shown to have a significant effect on Hg photoreduction in photocatalytic systems because it can form several complexes with Hg. The redox potentials for mercury chloride complexes are lower than divalent Hg as shown by the redox potentials (with the NHE as reference) in the graph below (Figure 2-2).
Recall that reduction of a metal ion is thermodynamically feasible if the standard reduction potential of that metal ion is greater than the energy associated with the conduction band-edge of the applied semiconductor. The greater the difference between the two, the greater affinity the compound has to be reduced. Therefore, divalent Hg will be reduced easier than chloride complexes. As chloride concentration increases, larger quantities of HgCl$_4^{2-}$ are present and Hg$^{2+}$ decreases and reduction becomes more difficult. Very high or low pH would then encourage the largest degree of Hg reduction. Chloride has also been hypothesized to block active TiO$_2$ sites by adsorption to the positively charged sites at pHs lower than the isoelectric point. 

Lastly, time of reaction is extremely important in Hg removal systems because if the Hg is exposed to the UV and catalyst too long it can reoxidize back to divalent Hg at acidic pHs. It is postulated that at these pHs there is a tendency for metallic Hg to be reoxidized due to the shift of the redox potentials of TiO$_2$. 

Figure 2-2. TiO$_2$ energy levels in relation to reduction potentials for various Hg species with respect to pH.
Photocatalyst with a solid substrate

In the design of a photoreactor system, the catalyst can be applied as a suspended or supported material. Generally, in the literature, TiO₂, one of the most commonly applied semiconductors, is tested as suspended particles in contaminated fluid. While this configuration is most often the most efficient, TiO₂ nanoparticles can be difficult to separate from solution. To overcome this barrier, TiO₂ has been immobilized with a solid substrate or coated onto various materials. Examples of such supports include glass⁸⁵, plastic⁸⁶, ceramic, and metal packing material⁸⁷, activated carbon⁶⁸, carbon nanotubes⁷⁴, optical fibers⁸⁸ and more.⁸⁹ When choosing a photocatalyst support several attributes should be considered: transparency to UV radiation, posses strong bonding capabilities without hindering reactivity, advantageous surface area, adsorption capacity for the compound of interest, enable less energy intensive solids separation, favor mass transfer, and be chemically inert.⁹⁰ A popular support that meets many of these considerations and has been well applied is silica gel.¹¹⁻¹³,¹⁵⁻¹⁷,⁹¹⁻⁹³

Sol-gel Silica

The sol gel process begins with liquid precursors that form a solid through hydrolysis and condensation reactions. The properties of the final solid are intricately dependent upon multiple parameters in the system. A set of terminology has been assigned to the sol-gel synthesis and are as follows below:⁹⁴

- Sol: a stable dispersion of solid colloidal particles
- Colloidal: a size greater than 1 nm and less than 1um (less than 1nm generally are solvated species)
- Gel: a continuous solid skeleton consisting of colloidal particles or polymers surrounded by a continuous liquid phase
- Gelling: time at which particles are linked together in branched chains where liquid is retained by capillary forces
• Coagulation: time at which particles aggregate and settle as a dense concentrated particulate
• Flocculation: time at which particles aggregate and link together
• R ratio: ratio of moles of water to moles of silicon alkoxide

Many silica precursors can be used to make a sol-gel, however, silicon alkoxides such as tetaethoxy orthosilicate (TEOS) and tetramethoxy orthosilicate (TMOS) are desirable because they contribute to better purity and control of colloid formation and growth. TMOS will hydrolyze very rapidly but in doing so will produce toxic methanol and is time limited in the condensation step. TEOS hydrolyzes slower but produces ethanol which is less toxic than methanol to the face and lungs so is often the precursor of choice.95-98 When using an alkoxide precursor, hydrolysis is the first chemical reaction step in the sol process where silicon atoms in the alkoxide experiences nucleophilic attack by water. Silicon alkoxides are generally not completely water soluble, so alcohol is added as a cosolvent. However, too much alcohol can be added and impede the condensation reaction due to competition for the active silanol sites which can cause re-esterification. The rate of hydrolysis is directly related to the rate of mixture homogenization. Hydrolysis reaction is shown (Equation 2-18):

\[-Si - OR + H_2O \rightarrow -Si - OH + ROH\]  (2-18)

The reaction is first order with respect to silicate and second order with respect to water. The reaction can be catalyzed by an acid or base;99 acid catalysis increases the hydrolysis rate whereas base catalysis is more beneficial for condensation. With acid catalysis, the alkoxide group is first protonated to remove the electron density away from the silicon to allow the nucleophilic attack by water. When gels are prepared with TEOS, hydrofluoric acid (HF) can increase gelation time by 100 times, and 10 times that of other acid or base catalyzed reactions.98 The catalysis can be attributed to the ability of the fluoride ion to increase the coordination and
reduce the electron density of silica atoms making it susceptible to nucleophillic attack. Hydrofluoric acid does however, reduce the hydroxyl content and reaction to heat treatment in addition to the catalyst effect. In general, the number of silanol groups corresponds to the adsorptive capacity of the silica-gels.

Once hydrated silica tetrahedra are formed, they can, in turn, react with one another in condensation reactions (Equation 2-19 and 2-20):

\[
-Si - OH + HO - Si^- \rightarrow -Si - O - Si + H_2O \quad (2-19)
\]
\[
-Si - OR + HO - Si^- \rightarrow -Si - O - Si + ROH \quad (2-20)
\]

Two silanols condense to form a Si-O-Si bond (siloxane). Similar reactions occur with a silanol and an unreacted alkoxy group. Polycondensation additionally links silica to form a network of siloxane bonds which ultimately make up the bulk structure of the silica gel. Re-esterification can occur when the hydrolysis and condensation reactions occur in reverse creating residual alkoxide groups. This is generally more prevalent in acid catalyzed, low R ratio (ratio of moles of water to moles of silicon alkoxide) and high alcohol content gels.

Condensation reactions continue and after a certain time (dependent on many factors), the sol gels. Gelation is marked by the condition of the sol no longer pouring (acting like a liquid) when it is tipped. The network will continue to further react until all the links are joined. The gelation time is susceptible to many conditions and therefore has not been marked as a distinct time.

After gelation, the gel is aged. Reactions continue, creating stronger network connections, causing the material to shrink and expunge liquid in a process called syneresis. In addition to condensation and syneresis, coarsening or “Ostwald ripening” occurs. Coarsening can have a large effect on the pore structure of a gel since small pores are filled in and large ones are spared. All of these processes serve to strengthen the sol and prepare it for drying.
In the drying phase, the liquid is expunged from the system. Capillary stresses caused by this “emptying of the pore network” cause cracking, unless the drying conditions are well controlled. Water retained on the surface of the silica can be in the form of silanol groups or adsorbed water. Silanol groups can be any of the following:

- Single silanols – on silica tetrahedra with 3 siloxane (Si-O-Si bonds)
- Geminal silanols – 2 silanols on the same silica tetrahedral with 2 siloxane bonds
- Vincinal silanols – 2 silanols on adjacent silica tetrahedral and hydrogen bonded to one another
- Structurally bound – silanols remaining in the bulk

Two drying processes are frequently used to create xerogels and aerogels. Xerogels are produced when the drying process includes temperatures below that of the critical temperature of the liquid in the pores. These gels experience a large decrease in surface area by loss of pore volume when high capillary forces caused by the surface tension of the solvent exiting the pores collapses many of those pores. On the other hand, heating above the critical temperature which eliminates capillary pressures will produce an aerogel. Aerogels do not experience shrinkage as in the case of the xerogel and are extremely porous but fragile.

Using adsorption/desorption isotherm characterization, silica gels generally fall under the Type I isotherm, also called the Langmuir Isotherm, characteristic of microporous materials with a small external surface area. Surface areas of the material are dependent upon pore size and can range from low to several hundred m²/g. Additional material characteristics that can be quantitated are the point of zero charge (PZC) and the isoelectric point (IEP). Values of 2-3 and 1-1.5 respectively have been measured.
Titania Immobilized with Silica

Several options are available for immobilizing TiO$_2$ photocatalyst with silica. Generally, TiO$_2$ is added to the surface or intermixed with the silica matrix. For example, TiO$_2$ can be grafted to the surface of mesoporous silicas using an inorganic or organometallic precursor. Silica pore clogging and ineffective clustering of TiO$_2$ can be problematic with this approach and has to be overcome using surfactants or other methods.$^{104}$ When intermixed into the silica matrix, the mixed material is often referred to as a SiO$_2$/TiO$_2$ composite. Various synthesis routes have been developed for SiO$_2$/TiO$_2$ composites, with the most popular method being sol-gel hydrolysis and condensation of organometallic precursors.$^{91,93}$ The resulting mixed oxides have varying chemical and physical properties depending on synthesis conditions.

Adsorption/Desorption Characterization of Porous Materials

Surface area and porosity of solids significantly define the adsorption phenomena of the material. It is therefore essential to characterize these properties to facilitate understanding of the adsorption process. Even before the 1800s, scientists observed that certain materials could adsorb volumes of gas larger than the volume the material occupied. Additionally, different gases would be taken up in different volumes. Then in the first half of the 19$^{th}$ century Saussure and Mitscherlich had theorized that the uptake of gas by solid materials was dependent upon the exposed surface of the material and the size of the pores.$^{105}$ These concepts remain two of the most important material properties for characterizing adsorption.

The quantity of gas adsorbed is a function of the mass of sample, temperature ($T$), vapor pressure ($p$), and characteristics of the adsorbate and adsorbent. A very simple equation for the amount of adsorption as moles of gas per gram of solid ($n$) would then be (Equation 2-21):

$$n = f(p, T, gas, solid)$$  \hspace{1cm} (2-21)

Then, for a constant temperature, gas, and solid (Equation 2-22):
\[ n = f(p)_{T,\text{gas, solid}} \]  

(2-22)

Finally, if the constant temperature is that of one below the critical temperature of the gas (Equation 2-23):

\[ n = f\left(\frac{p}{p_0}\right)_{T,\text{gas, solid}} \]  

(2-23)

Equation 2-23 is the foundation for the adsorption isotherm. The isotherm is a plot of the volume of gas adsorbed (n) at a constant temperature over a series of relative pressures \(\frac{p}{p_0}\).105

**Measurement**

This theoretical equation has been translated into a measurement technique. The typical procedure for nitrogen adsorption begins by outgasing the solid sample in a fixed volume glass tube to remove adsorbed material. Contaminants can occlude pores and negatively affect the measurement process. Physisorbed materials, such as adsorbed water, can be removed under a vacuum at elevated temperatures. Exact conditions will depend on the solid sample. The solid is then connected to a gaseous nitrogen source that is added or removed in finite volumes at controlled pressures. The temperature is held constant at the critical temperature of the gas (about 77 K) by a bath of liquid nitrogen. The end result is a data plot of the quantity of adsorbed gas versus the relative equilibrium pressure reached.

The amount of adsorbed gas can be determined by gravimetric, volumetric, or thermal conductivity measurements. By the gravimetric method, the mass of adsorbed gas is measured by a high precision balance. The volumetric method uses gas laws to relate changes in the volume of the gas introduced to a fixed volume which holds the solid sample. Therefore, this measurement technique requires high precision pressure transducers and volume measurements. This method is most frequently used with nitrogen adsorption. Thermal conductivity measurement has a cell that detects changes in thermal conductivity of a gas stream that passes
over the solid sample which changes as adsorption occurs. While gravimetric is the most accurate method, it is very costly and more difficult to maintain the equipment. The thermal conductivity method is often forgone due to the slower measurement process. Therefore, volumetric analysis is the most popular.\textsuperscript{106}

**Classification**

After obtaining the data for an adsorption isotherm, much can be inferred about the material based on a visual inspection of the isotherm plot. As can be imagined, the endless number of solids and several types of gases to adsorb to them presents an innumerable amount of possible isotherms to analyze. However, in 1940, Brunauer, Deming, Deming, and Teller published a classification of all physical adsorption isotherms by generalizing them into five types.\textsuperscript{107} While two types were already well identified, the Langmuir adsorption isotherm and S-shaped or sigmoid isotherm, three other types were classified then. Several years following, the International Union of Pure and Applied Chemistry (IUPAC) adopted the five types and additionally classified a sixth.\textsuperscript{108} An illustration of each of the isotherms are shown in Figure 2-3. A description of the isotherms and what can be deduced from them is as follows:\textsuperscript{105,109,110}

- **Type I:** This isotherm is often referred to as the Langmuir isotherm. It is concave with respect to the $P/P_0$ axis and reaches a limiting value. Pre 1960’s, this isotherm was thought to be typical of monolayer coverage. Based on arguments by a number of investigators, it is now generally accepted that Type I isotherms are indicative of microporous solids with a low external surface area, such as activated carbon, zeolites, molecular sieves and some silica gels that experience micropore filling.

- **Type II:** This isotherm is characterized by unrestricted surface adsorption. An inflection point (called point “B”) can be seen where the curve changes from concave, with respect to the $P/P_0$ axis, to convex and represents where the monolayer coverage finished and the multilayer adsorption began. Solids that demonstrate this type of isotherm are non-porous or macroporous.
- **Type III**: This isotherm is convex to the $P/p_0$ axis. This type occurs when the adsorbent-adsorbate interactions are weak with respect to the adsorbate-adsorbate interactions.

- **Type IV**: This isotherm has a steep slope at high relative pressures which is indicative of capillary condensation. This generally occurs for mesoporous solids.

- **Type V**: This isotherm is similar to type II but also contains mesopores indicated by the steep slope of the middle section.

- **Type VI**: This isotherm has stepwise multilayer adsorption.

---

**Figure 2-3. Gas adsorption isotherms as classified by IUPAC**
These six classes of isotherms are of course not the end all. Several variations do exist, but most of the five classes do remain well defined and frequent. A further note on Types II and V are that they do not exhibit the same desorption curve as their adsorption curve. When this occurs, it is termed hysteresis. Hysteresis will be explained further in the following sections.

**Surface area analysis**

The combination of isotherm measurement with adsorption models can result in surface area and pore size analysis. Theoretically, if the amount of adsorbate covering the adsorbent at monolayer coverage ($n_m^a$ in moles) and the area taken up by each adsorbate ($a_m$) is known, the surface area ($A_s$) can be calculated as Equation 2-24:

$$A_s = n_m^a L a_m$$

(2-24)

where L is Avogadro’s constant. However, this scenario is very infrequently the case.

Therefore, much attention has been focused on how to analyze the isotherm data to produce desired information about the adsorbent surface area and pore structure.

The BET method, developed in 1938 by Brunauer, Emmett and Teller,\textsuperscript{111} is the most widely used procedure for surface area analysis of solids. This method assumes a particular model for physisorption. The assumptions simplify the model for ease of use, but in turn can reduce the accuracy of the model. The BET method assumes that the adsorbent has uniform adsorption sites which are occupied randomly, there are no lateral interactions between adsorbate molecules, molecules in the first monolayer act as sites for the second layer and the same for subsequent layers, and that after the first layer coverage, all other layers have liquid-like properties.\textsuperscript{112} The BET method is determined by nitrogen adsorption experiments at the boiling point of $N_2$ (about 77 K) over a range of relative pressures less than and equal to 1.

The primary equation (Equation 25) which is used is:
\[
\frac{1}{W[(P_0/p) - 1]} = \frac{1}{W_mC} + \frac{c-1}{W_mC} (P/P_0)
\]  

(2-25)

where \(W\) is the weight of the adsorbed gas at \(P/P_0\), \(W_m\) is the weight of the adsorbate at monolayer coverage, and \(C\) is the BET constant. \(C\) is related to enthalpy of adsorption of the monolayer and therefore is an indication of the interaction forces between the solid and gas. The constant needs to be sufficiently high to indicate attraction between the adsorbate and adsorbent to achieve monolayer coverage before subsequent multilayer formation for the BET equations to represent correct surface area calculations. At a \(C\) value less than 20, Point B (Figure 2-3) of the adsorption isotherm cannot be distinguished, but above a value of 100, it will be very clear. However, once the value exceeds 200, micropore filling has likely occurred. Generally, in a relative pressure range around 0.05 to 0.30 for mesoporous materials, a straight line can be drawn through the points on a plot of the measured \(\frac{1}{W[(P_0/p) - 1]}\) versus \(P/P_0\) as seen in Figure 2-4.

![BET plot to calculate weight of monolayer (\(W_m\))](image)

**Figure 2-4. BET plot to calculate weight of monolayer (\(W_m\))**

The slope (\(s\)) (Equation 2-26) and intercept (\(i\)) (Equation 2-27) of this line can be used to calculate the value of \(W_m\) (Equation 2-28).

\[
s = \frac{c-1}{W_mC}
\]

(2-26)
\[
i = \frac{1}{W_mC}
\]
\[
W_m = \frac{1}{s+i}
\]  

Using the data from Figure 2-4 as an example, the value of \(W_m\) is 0.087 g using the slope of 11.37 and the intercept of 0.112. Additionally, \(C\) can be calculated from the slope and intercept with Equation 2-29.

\[
C = \frac{s}{i} + 1
\]  

Again referring to the data in Figure 2-4, the \(C\) constant would equal approximately 100 which is a good \(C\) value for a mesopore range. From here, the surface area \(S_t\) of the solid can be calculated from Equation 2-30:

\[
S_t = \frac{W_mC_Acs}{M}
\]  

\(N\) is Avogadro’s number, \(A_{cs}\) is the cross sectional area of the adsorbate molecule, and \(M\) is the molecular weight of the adsorbate. As mentioned previously, nitrogen is often used as the adsorbate and is the chosen adsorbate for this discussion. \(A_{cs}\) of nitrogen is 16.2 Å² in a hexagonal close packed arrangement at 77 K and M=28 g/mol.\(^{109}\)

**Pore Analysis**

Porosity is generally described by both pore size and volume. The combination of the two gives a good depiction of the nature of porous adsorbent. Both variables can be analyzed with the same adsorption isotherm data over a range of relative pressures up to the limiting \(P/P_0 = 1\) that is used for surface area analysis.

**Pore volume**

The total pore volume can be determined by relating the total amount of gas adsorbed at the limiting pressure to the mass of the adsorbent exposed to the adsorbate. This requires the assumption that all of the pore space is filled with liquid adsorbate. For mesoporous materials,
the slope of the adsorption isotherm should reach a plateau near the limiting pressure indicating that the pores are filled.

**Pore size**

The entirety of the pore volume will be distributed over various pore sizes which can be represented by a pore size distribution. The size of pores is important for understanding molecule diffusion into the porous network and adsorption behavior. IUPAC classifies pores according to their width. Those exceeding 500 Å (50 nm) are macropores while less than 20 Å (2 nm) are considered micropores and those in-between are mesopores. Each size range corresponds to characteristic adsorption important for analysis. For the scope of the work, emphasis will be on the mesopores. Qualitative analysis can be accomplished by inspection of the adsorption isotherm. As a generality, various relative pressures can be related with sequences of gas adsorption. Table 2-1 demonstrates the relationship:

<table>
<thead>
<tr>
<th>P/P0 Range</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0.10</td>
<td>Micropore filling</td>
</tr>
<tr>
<td>0.01 – 0.10</td>
<td>Sub-monolayer formation</td>
</tr>
<tr>
<td>0.05 – 0.30</td>
<td>Monolayer formation</td>
</tr>
<tr>
<td>&gt;0.20</td>
<td>Multilayer formation</td>
</tr>
<tr>
<td>&gt;0.35</td>
<td>Capillary condensation</td>
</tr>
</tbody>
</table>

Using the table as a guide, an adsorption isotherm can be observed based on the slope of the line in these pressure ranges indicated. A large slope indicates the dominance of a mechanism in that range. Micropore filling is the dominant feature for microporous materials, while capillary condensation is signature of mesoporous materials and macroporous materials will continue to have a large slope up to unity gas pressure. On this basis, the interaction of the adsorbate and the material can provide insight into the porous nature. Determining the quantitative pore size distribution becomes more complicated by involving several computations.
and requiring assumptions to be made about pore shape and network, mechanism of pore filling, validity of equations and so on.\textsuperscript{109}

**Kevin equation**

The Kelvin equation is the basis of most pore size calculation methods in the mesopore size range. Its theory was developed by William Thomson (later, Lord Kelvin) to explain, thermodynamically, how condensation of a vapor to a liquid can occur in pores despite a relative pressure less than one. The pore walls have to be a certain distance apart to serve as nucleus for condensation. The original equation was adapted specifically for adsorption data and resembles Equation 2-31:

\[
\frac{1}{r_1} + \frac{1}{r_2} = \frac{-RT}{\sigma v} \ln \left( \frac{P}{P_0} \right)
\]

where \(r_1\) and \(r_2\) are the principal radii of curvature of the liquid meniscus in the pore at a given relative pressure, \(\sigma\) is the surface tension of the adsorbate (nitrogen at 77 K = 8.85 ergs/cm\(^2\)), \(v\) is the molar volume of the adsorbate (liquid nitrogen = 34.7 cm\(^3\)/mol), \(R\) is the gas constant (8.314 x 10\(^7\) ergs/deg-mol) and \(T\) is the boiling point of nitrogen (77.4 K). From this equation, pore shape and meniscus curvature has to be assumed. Generally a hemispherical meniscus is assumed and either cylindrical pore shape \((r_1 = r_2)\) or slit-shaped \((r_1 = \text{width and } r_2 = \infty)\).

Equation 2-32 illustrates a case with cylindrical pores:

\[
r_K = \frac{-2\sigma v}{RT \ln \left( \frac{P}{P_0} \right)}
\]

where \(r_K\) is the Kelvin radius which replaced \(r_1\) and \(r_2\). As gas is adsorbed to the solid, the nominal radius of the pore is decreased. The actual pore radius is then continually decreasing and can be calculated as the Kelvin radius minus the thickness of adsorbed gas. For slit-shaped pores, the Kelvin radius would be half that of the cylindrical pore.\textsuperscript{109} This formula describes how capillary condensation occurs in wettable pores of sufficiently small radii. Many other
calculation methods for determining pore size distribution have been developed since the Kelvin equation, but all still assume validity of the Kelvin equation.\textsuperscript{112}

**Hysteresis Loops**

Identification of a hysteresis loop begins with inspection of the gas adsorption isotherm. As mentioned previously, the hysteresis can be seen when the adsorption and desorption curves of the isotherm do not follow the same path. The cause of this loop can be attributed to many things which are still under debate today. It is under general consensus that when a hysteresis loop occurs in the multilayer range of a gas adsorption isotherm, it is associated with capillary condensation in mesopores.

**Early theories**

The cause of the hysteresis loop has been under debate for many years. Early on, Zsigmondy proposed that incomplete wetting during adsorption causes a higher equilibrium vapor pressure. Therefore, the relative pressure for the same amount of adsorbed gas is higher for the adsorption curve than the desorption branch as is always true of hysteresis loops.\textsuperscript{113} Alternatively, Kraemer and McBain support the theory of ink-bottle shaped pores. In this instance, gas fills during adsorption and condenses first in the narrow neck then extends to the larger body at high relative pressures then during desorption, evaporation of the adsorbate in the wide pore body is delayed until the thinner pore neck empties at a lower relative pressure. This theory did not agree with earlier theories by hypothesizing that a delayed meniscus was possible in the desorption curve of the isotherm.\textsuperscript{114,115} Shortly after, Foster and Cohan supported the idea that hysteresis was the result of a delayed meniscus formation in capillary pores by manipulation of the Kelvin equation. The basis of their idea supported that hysteresis would (1) occur for all open capillary materials with complete wetting, (2) not occur for closed tapering capillaries or capillaries with a diameter less than four times the adsorbed film, (3) could occur with small
adsorbates but not with larger ones, which has been noted in experimental studies, and (4) would always occur with incomplete wetting caused by surface contamination.116

**Shape**

In 1958, de Boer speculated that the shape of the hysteresis loop was related to the shape of the pores.117 He grouped hysteresis loops into five characteristic types based on the isotherm slopes. The following describe the general hysteresis loops:106,117

- **Type A:** This can be identified by two steep slopes of both the adsorption and desorption curves of the adsorption isotherm at intermediate relative pressures. It is an indication of capillary tubes open on both ends, wide ink-bottle pores, and wedge shaped capillaries.

- **Type B:** This type has a steep adsorption curve slope near the saturation vapor pressure. Generally, open slit-shaped pores with parallel walls and ink-bottle pores exhibit this type of hysteresis loop.

- **Type C:** Here, the adsorption curve is steep at intermediate pressures and the desorption curve is sloping. This is typical of capillary tubes with open ends.

- **Type D:** This type exhibits a steep adsorption curve at the saturation vapor pressure but with a sloping desorption curve. This occurs for heterogeneous pores with wedge-shaped capillary tubes open on both ends, and capillary tubes with wide bodies and narrow necks.

- **Type E:** This has an adsorption branch with a sloping curve and a steep desorption branch at intermediate relative pressures. This type is similar to Type A, and is associated with ink-bottle shaped pores or interconnected capillaries.

After some time, IUPAC recommended the use of four types of hysteresis. The most commonly found loops classified by de Boer, Type A, B, and E were renamed to Type H1, H3, and H2 respectively and a fourth, Type H4 was added (Figure 2-5).

Type H1 and H4 represent extremes while Type H2 and H3 are intermediates. IUPAC determined that Type H1 indicates uniform spheroid particles that result in a narrow pore size range. Type H3 has been associated with aggregates of plate-like particles which have slit-shaped pores. Type H4 is similar to Type H3 with narrow slit-shaped pores, but in addition, shows microporosity. Lastly, Type H2 is very common for porous adsorbents, but remains
extremely difficult to interpret. The role the pore network plays in changing the shape of the hysteresis loop is not well understood. So while in the past, Type H2 was believed to be associated with ink bottle pores (narrow necks and wide bodies), this is now uncertain due to the impact the pore network might have. Hysteresis loops caused by mesopores should close above a relative pressure of 0.4 when using nitrogen adsorption. This relative pressure is at the lower limit of capillary condensation since the condensate (nitrogen) will be below its critical pressure. Also seen in Figure 2-5 are dotted lines. These lines indicate low pressure hysteresis. Mostly, systems that exhibit this phenomenon are microporous.

Later, in 1967, Brunauer et al. suggested that capillary condensation does not occur at the same relative pressure as capillary desorption. The work supported the use of adsorption and desorption curves based on the type of model used for the analysis. In summary, hysteresis phenomena became recognized as being based on theory on a pore by pore basis or on a pore network basis.

Figure 2-5. IUPAC classifications for hysteresis loops
Condensation in a single pore

One direction of theories is on the pore level. Hysteresis could be assumed to be caused by the delay of the vapor/liquid transition due to persistence of metastable states of the adsorbate. This could occur as either the delayed condensation of gas adsorbate during adsorption or the delayed evaporation of the liquid adsorbate during desorption in each pore to produce a combined effect.\textsuperscript{119}

Interconnectivity of a real pore network

In 1982, Mason theorized that Type H2 hysteresis was the result of interconnected pores with or without single pore hysteresis. He hypothesized that during adsorption, interconnected pores all had exposure to the vapor phase and would fill based on their particular size. However, under desorption conditions, for a pore to empty it has to first come in contact with the vapor phase. This will happen based on the interrelationship of pore connectivity and pore size. Once the outer pore space empties a chain of reaction occurs to empty the inner pores which is illustrated by the sharp change in slope of the desorption curve.\textsuperscript{120}
CHAPTER 3
MATERIALS AND METHODS

Chemicals and Materials

All reagents used in this work were of analytical grade and were used without further purification. Hg solutions were prepared prior to each experiment through dilution of a 1,000 mg/L Hg(NO₃)₂ standard solution (Fisher Scientific) with deionized water (18.2 MΩ-cm). Solutions of HgCl₂ and C₄H₆O₄Hg (Hg(OAc)₂) were also used when notated. Here, the Hg solution was prepared through dissolution of the solid to make a concentrated stock solution followed by dilution of this stock solution with deionized water as the matrix for both solutions. The pH of obtained solutions were not adjusted and exhibited a value of about 4 ± 1 and did not vary more than 1 pH unit from the initial after testing.

Materials Synthesis

Sol-Gel Methodology

Silica gels were produced via an acid-catalyzed sol-gel method using tetraethyl-orthosilicate (TEOS) as the silica precursor. Nanopure water (18.2 MΩ-cm), ethanol (Fisher, 200 proof), 1 M nitric acid (diluted from concentrated Fisher, certified ACS) were added to the TEOS using the volumes described in Table 3-1 which shows the exact volumes used to create one batch of silica gel which is equivalent to about 20 g of final product. The liquid volumes were added in the order listed and mixed in a polystyrene container with a magnetic stir bar. By varying the volume 3 %wt HF (diluted from 49 % Fisher, certified ACS) pore diameters could be manipulated. STCs were produced in the same manner by adding various masses of the photocatalyst, DP25, to the liquid precursors. A discussion of the change in physical characteristics with change in HF and TiO₂ will ensue. Nomenclature for the materials is based on these variables, specifically the volume ratio of 3 %vol HF to 1 M nitric acid and the mass ratio
of TiO$_2$ to STC. For example, STC-0.25-30 represents a STC with 0.25 mL of 3%$_{\text{vol}}$ HF to 1 mL of 1 M nitric acid and 30 mg of TiO$_2$ per 100 mg of dry composite while silica-0.25 would represent the same material with the absence of TiO$_2$.

Table 3-1. Silica gel liquid precursors

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEOS</td>
<td>70</td>
</tr>
<tr>
<td>Nanopure water</td>
<td>50</td>
</tr>
<tr>
<td>Ethanol</td>
<td>100</td>
</tr>
<tr>
<td>1 M nitric acid</td>
<td>4</td>
</tr>
<tr>
<td>3% hydrofluoric acid</td>
<td>2 – 16*</td>
</tr>
</tbody>
</table>

* varied to control pore size

Gelation time for the sols was dependent upon concentration of HF since it catalyzes hydrolysis and condensation reactions$^{94}$ and ranged from approximately 15 minutes for STC-2-0 to over 8 hours for STC-0.25-0. After gelation occurred (when the sol no longer pours) and a monolith resulted, the polystyrene containers were capped and taped to prevent evaporation losses. After two days of room temperature storage in this fashion, the containers were moved to a mechanical oven which held the temperature at 65 $^\circ$C for 48 more hours to complete the aging process. Lastly, the sol was removed from the polystyrene containers and crumbled into Teflon screw cap jars. These containers each have a small pin sized hole in the lid to allow liquid to escape the pores as a vapor. This helps prevent pore collapse by reducing capillary pressure in the pore. The jars were heated using a temperature ramping program, 18 hrs at 103 $^\circ$C followed by 6 hrs at 180 $^\circ$C. After the drying process was complete, the silica and STC materials were ground using a mortar and pestle. The ground material was sieved to accomplish a primary particle size distribution of 45 to 90 μm to be used in batch tests. After preliminary tests using samples that had been dry sieved and stored at ambient laboratory conditions showed poor reproducibility, a new sieving procedure was developed to try to increase the homogeneity of the selected material size. The chosen fraction was rinsed for approximately 5 minutes with a stream
of DI water to rinse off smaller attached particles (mainly of concern was TiO$_2$), reduced fluoride content, increase pH stability and removed any soluble organics. The wet particles were transferred to a glass sample vial and dried at 110 ºC then capped with a Teflon lined lid and stored in a dark desiccator. Before using, the sample was additionally heat treated at approximately 100 ºC overnight to remove any adsorbed water which would add false mass to the sample in experiments. This procedure was also used to produce a primary particle size fraction of 6 to 45 µm.

Additionally, some prepared STCs were further calcined in a programmable muffle furnace (Barnstead Thermolyne 47925-80). The program followed a 5 ºC/min ramp up to the desired temperature, held for 2 hours and then cooled gradually. A temperature of 450 ºC and treatment time of 2 hours were found to be the optimal combination for removal of residual organic material from the composites. When using the composites for organic compound mineralization, it is imperative for that STC do not contribute to the concentration of total organic compounds that would interfere directly with the test results.

To facilitate use in a continuous flow column, the liquid sol was poured into 96-well assay plates shortly before gelation occurred. The aging process was carried out in foil wrapped and taped assay plates. After aging, the gel had formed cylindrical shaped pellets which were removed from the plates and placed in the Teflon drying containers. The drying process was performed for these pellets just as had been completed for the crumbled monolith. The resulting pellets were also washed with deionized water before using in the column configuration.

**Titania Production**

Many different synthesis methods have been used to produce TiO$_2$ nanomaterials. These conditions impact titania phase composition, crystalline size distribution, degree of aggregation, surface area and surface adsorption properties. A handful of synthesis methods previously used
in the literature were undertaken to produce TiO$_2$ materials with a greater surface area and more surface functionality over that possessed by DP25. The first two procedures used an organometallic Ti precursor. SA(450) was produced via a mixture of 9 mL TTIP (titanium isopropoxide) (Fisher Ti(OCH(CH$_3$)$_3$)$_4$) dissolved into 4 mL anhydrous ethanol (Pharmco-Apper 99.98%) that was added dropwise to 100 mL of an ethanol-nanopure water solution (1:1) under stirring$^{121}$. An alternative to TTIP was TPT (tetra-isopropyl titanate) (Dupont Ti(OC$_3$H$_2$)$_4$). This precursor (35.8 g) was dissolved into 100 g anhydrous isopropanol (Fisher ACS grade) was added dropwise to 100 g of nanopure water plus 5 g of monoethanolamine under stirring.

Titanium salts can also be used to produce TiO$_2$. QHZ(450) was produced using a precipitation reaction of TiCl$_4$$^{122}$. A mixture of 375 mL nanopure water and 25 mL TiCl$_4$ were prepared at 4 $^\circ$C in an ice bath. Concentrated ammonia (Fisher NH$_4$OH) was added until the pH of the solution reached 7. The solution temperature was brought up to 20 $^\circ$C and held for 1 hour. For all procedures, centrifugation was used to separate precipitated TiO$_2$ from the suspension. The collected solids were rinsed with ethanol, separated, and dried at 100$^\circ$C. Resulting media was separated using a mortar and pestle then calcined for 2 hours at 450 $^\circ$C. QHZ was also produced without calcination.

The produced materials were characterized for surface area and functionality and applied for Hg removal. Further, QHZ was immobilized in a silica support in the same manner as mentioned above but substituting the newly produced TiO$_2$ for DP25 and tested as STC-2-60QHZ.

**Material Characterization**

Several characterization methods were employed to further understand the STC materials specifically produced in this research. Secondary electron images were collected using a JEOL JSM 6335F scanning electron microscope (SEM) at 5 kV accelerating voltage. Nitrogen
adsorption-desorption analyses were conducted using a Quantachrome Autosorb 1C-MS gas sorption analyzer. STC samples were outgassed for 24 hours at 180 °C. Alternatively, a Quantichrome NOVA 1200 gas sorption analyzer was also employed for some materials. The source of the data is specified. Specific surface area values from either instrumentation were determined using the BET model with nitrogen adsorption data (P/Po = 0.1 to 0.3). Total pore volume was determined by nitrogen adsorption at P/Po = 0.99. Equation 3-1 was used to calculate the average pore size of the STC:

\[ d = \frac{4 \times V_p}{S} \]  

(3-1)

where \( d \) is average pore diameter, \( V_p \) is total pore volume, and \( S \) is specific surface area. A duplicate run was less than 5% different than original results. Alternatively, BET surface areas and average pore size (using the Kelvin equation) were measured using the same method as just reviewed but using a Quantachrome NOVA 1200 Gas Sorption Analyzer. Presentation of these results will describe which instrument was used.

Streaming potential measurements were made using a Paar Physica Electro Kinetic Analyzer. Zeta potentials were calculated using a measured voltage drop across a packed bed of STC as a 0.001 M KCl solution was flowed through the bed at varying pressures. The solution was titrated with 0.1 M HCl to achieve an estimation of the isoelectric point (IEP). Here, the STC was not ground and was used in the bed as larger size particles between 2 and 8 mm. Before analysis, the instrument was zeroed using a clean cotton sample. A minimum of 6 pH values were analyzed with 8 replicate measures at each pH value to produce an average zeta potential reading. Linear regression was fitted to each set of points to determine the IEP and resulted in an \( R^2 > 0.95 \). A duplicate run was less than 5% different confirming reproducibility of the test.
Diffuse reflectance allows estimation of the bandgap energy, or photon energy necessary to initiate photocatalytic reactions. Past work has demonstrated the importance of bandgap energy and its relationship to semiconductor particle size and photocatalytic activity. By using the Kubelka-Munk parameter (Eq. 2) where $R$ is the proportion reflected, $h$ is Planck’s constant, and $\nu$ is the frequency of light, the band gap can be determined. Diffuse reflectance measurements were performed using a Labsphere PELA-1000 integrating sphere module in a Perkin-Elmer Lambda 800 UV/vis spectrophotometer. Plots of the Kubelka-Munk parameter (Equation 3-2) were used to determine bandgap energy by defining a linear model for the linear portion of the absorption transition using least squares regression ($R^2$>0.9) and extrapolating to zero at the corresponding photon energy.

$$\left(\frac{(1-R)^2}{2R} \times h\nu\right)^{\frac{1}{2}}$$

(3-2)

Further TiO$_2$ analysis was performed with powder X-ray diffraction patterns using a Phillips APD 3720 with Cu Ka radiation with 2Θ of 20-80° with a step of 0.02°. Particle size comparisons were made using the Scherrer equation (Equation 3-3). A shape factor (k) of 0.9, wavelength of the CuKα1 x-ray source (λ) of 0.1541 nm, and an anatase 101 peak (2θ) of 25.4 were used for all calculations. In order to account for uncertainty in measurements only those peaks greater than 3σ of the baseline noise were utilized.

$$t = \frac{k\lambda}{B \times \cos \theta}$$

(3-3)

Available TiO$_2$ surface areas of the STCs were determined with a procedure developed by Marugan et al. This procedure was based on the reaction of phosphonic acid with TiO$_2$ in a methanol solution, but not with silica. First, a methanol:water solution was made with a volume ratio of 4:1 and adjusted to pH four with concentrated HNO$_3$. This solution was used to make a 4 mM solution of phenylphosphonic acid. Phenylphosphic acid (C$_6$H$_7$O$_3$P), has been
characterized in the literature\textsuperscript{128,129} and has approximate dimensions of 11 by 8 by 16 Å.

Selected media was mixed in the phenylphosphonic acid solution for 24 hours (1 g/L mass loading). In this time period, phosphorous reacted with Ti-OH surface groups that were accessible on the material surface. The media was separated from the liquid using vacuum filtration through 0.45 μm PTFE filters. The solids were dried then a specific mass was digested with hydrofluoric acid.\textsuperscript{130} The digestate was analyzed using a Perkin-Elmer Plasma 3200 Inductively Coupled Plasma Spectroscopy (ICP-OES) system at a wavelength of 213.617 nm for phosphorous and 332.94 nm for titania. This ICP was equipped with two monochromators covering the spectral range of 165-785 nm with a grated ruling of 3600 lines/mm. Calibration standards were checked before and after each analysis set to confirm that systematic error was at a minimum. Phosphorous content was then correlated to the accessible TiO$_2$ surface area using the following two formulas (Equation 3-4 and Equation 3-5):

\begin{equation}
\text{Atoms P per nm}^2 \text{ TiO}_2 = \frac{\text{phosphorous content (mgP/g)}}{S_{\text{BET-TiO}_2} \text{ (m}^2/\text{g)} \times \left(1 \text{ m}^2/10^{18} \text{ nm}^2\right) \times \left(\frac{\text{gP/1000 mgP}}{30.974 \text{ gP}}\right) \times \left(\frac{\text{molP}}{6.022 \times 10^{23} \text{ mol P}}\right)}
\end{equation}

\begin{equation}
\text{m}^2 \text{ TiO}_2 / \text{g STC} = \frac{\text{phosphorous content (mgP/g)}}{\text{atoms P per nm}^2 \text{ TiO}_2 \times \left(1 \text{ m}^2/10^{18} \text{ nm}^2\right) \times \left(\frac{\text{gP/1000 mgP}}{30.974 \text{ gP}}\right) \times \left(\frac{\text{molP}}{6.022 \times 10^{23} \text{ mol P}}\right)}
\end{equation}

Two discrete samples of each material were analyzed. Detailed experimental methods can be also be found from the sources Mutin et al. and Marugan et al.\textsuperscript{127,131}

**Mercury Testing**

Since Hg is a difficult chemical to analyze at low levels,\textsuperscript{132} due care was taken in all sampling procedures. All vessels for storing Hg solutions or Hg analysis chemicals were made of glass and capped with Teflon lined lids. Glassware was washed in 25% nitric acid and rinsed copiously with deionized water before use. Total aqueous Hg concentrations were determined using the SnCl$_2$-reduction technique and detection by atomic absorption spectrometry per EPA standard method 254.3. The instrumentation used was a Teledyne Instruments Hydra Atomic
Absorption Mercury Analyzer manufactured by Leeman Labs. A minimum detection limit (MDL) was found to be 0.4 µg/L Hg. For all studies, Hg removal is reported as a normalized concentration, \( C/C_0 \), filtrate concentration over initial concentration both in µg/L Hg. Duplicate samples for each experiment were performed and error bars illustrate the range.

**Pseudo Equilibrium Batch Studies**

Various media loadings were studied at pseudo equilibrium. Hg solutions were contacted with adsorption/photocatalysis media (Silica and STCs were applied as synthesized at a primary particle size distribution from 45 to 90 µm while TiO\(_2\) was applied as received from the manufacturer) in filled 40 mL glass vials with Teflon lined lids for 24 hours at room temperature on a rotation device. Solution media slurries were vacuum filtered through a 0.45 µm mixed cellulose membrane filter. A 20 mL aliquot was withdrawn from the filtrate and stored in an acidified glass vial with a Teflon lined cap until being analyzed. The acidification was equivalent to the first step of the digestion process as outlined in EPA standard method 254.3.

Control samples were also filtered. The collected samples were analyzed for total Hg as described above less than 30 days from the time of collection.

**Kinetic Batch Studies**

Time study batch experiments were carried out in a cylindrical reactor which contacted 100 mL of Hg solution, continuously mixed by magnetic stirring, and a PL-S Twin Tube Short Compact Fluorescent Lamp of 254 nm or 365 nm (bulbs.com, Worcester, MA) (Figure 3-1). Ferrioxalate actinometry determined the total flux for each lamp into the surrounding solution to be \( 2.46\times10^5 \) einsteins/min and \( 1.25\times10^5 \) einsteins/min, respectively. If a dark (absence of any wavelength light) condition was studied, the UV lamp was not illuminated but did remain in solution to achieve the same mixing gradient. The reactor was also equipped with a ¼ inch glass purge tube and a glass vent port to enable an in-situ gas purge directly into the reactor solution.
when desired. When the purge was not applied, the glass tubes were sealed. During the contact time, the reactor was covered to shield the solution from ambient light. These reactions were studied for 5, 15, 30, and 60 minutes individually with the UV bulb illuminated (UV photocatalysis) or turned off (adsorption alone in the absence of light).

Media loading was selected to be 1 g/L based on data from the pseudo equilibrium studies. Here as well, silica and STCs were applied as synthesized at a primary particle size distribution from 45 to 90 µm while TiO₂ was applied as received from the manufacturer. When otherwise noted, however, a STC primary particle size distribution of 6 to 45 µm was applied. After the desired time elapsed, the solutions were vacuum filtered with a 0.45 µm mixed cellulose membrane filter to separate the media. A 20 mL aliquot was withdrawn from the filtrate and stored in an acidified glass vial with a Teflon lined cap until being analyzed. The acidification was equivalent to the first step of the digestion process as outlined in EPA standard method 254.3. Control samples were also filtered. The collected samples were analyzed for total Hg as described above less than 30 days from the time of collection.

![Figure 3-1. Schematic of the batch reactor used for adsorption alone and photocatalysis time studies](image)
Continuous Flow Column Studies

Hg removal was also studied in a continuous flow-through column (Figure 3-2). Here, an apparent volume of 27 mL of full size STC pellets were added to the column below. The column operated in continuous up-flow driven by a peristaltic pump with which the flowrate was adjusted to achieve a targeted empty bed contact time. Prior to testing with Hg solutions, the STC were washed with 4 L of deionized water per 10 g of material prior to introducing Hg laden solutions. This washing procedure removed residual water soluble TOC to less than 1 mg/L non-purgeable dissolved organic carbon and ensured that water adsorption by the pellets would occur prior to introducing Hg. The column was drained after rinsing. Following, an Hg solution of 100 µg/L was introduced to the column and the effluent from the column was sampled at even time intervals for Hg.

Figure 3-2. Schematic of continuous flow testing apparatus

In-Situ Purging

To study reactor conditions with a purge the batch reactor in Figure 3-1 was employed with a regulated gas flow of 2 L/min connected to the purge tube. This was the maximum flow rate that
could be achieved within the confines of the reactor. Purge gases, ultra high purity nitrogen, breathing grade air, and ultra high purity oxygen used for this purpose were acquired from Airgas, Inc.

Hg solutions were tested with several combinations of dark/UV254/UV365 and no purge/nitrogen purge/air purge/oxygen purge. After the desired reaction time elapsed, the lamp and cap were removed and an unfiltered 20 mL aliquot was withdrawn and stored in an acidified glass vial with a Teflon lined cap until being analyzed. The acidification was equivalent to the first step of the digestion process as outlined in EPA standard method 254.3. The remaining reactor solution (80 mL) was filtered through a 0.45 µm mixed cellulose membrane filter using vacuum filtration. A 20 mL aliquot of this filtrate was withdrawn and stored in the same manner as the unfiltered aliquot. The collected samples were analyzed for total Hg as described above less than 30 days from the time of collection.

Other Characterization

- The pH was measured with specific electrode on an accumet* Excel XL20 benchtop multiparameter meter. The meter was calibrated prior to use.

- Chloride concentrations were measured with a Hach reagent kit (method 8113) for the DR5000 spectrophotometer.

- Fluoride measurements were taken with a selective electrode (Accumet catalog No. 13-620-528). The electrode measures free Fluoride at concentrations of $10^{-5}$ M to saturation. All standards and samples were buffered with total ionic strength adjusting buffer (TISAB) to eliminate differences in ionic strength and prevent polyvalent cation-fluoride complexes or hydroxide ion interferences.

- Non-purgeable dissolved organic carbon (reported as TOC) was analyzed on a Tekmar-Dohrmann Apollo 9000HS with autosampler. Samples were pH adjusted with phosphoric acid followed by zero-grade air purging to strip inorganic carbon before the sample is sent to the furnace. The furnace employs high temperature (680 ºC) oxidation on a platinum/alumina catalyst. After, water is condensed in a cooling coil and remaining water is removed with a Nafion membrane. Corrosives are scrubbed with a Cu/Sn scrubber, and then the CO₂ is determined with an NDIR detector.
**Kinetic Modeling**

To compare the reaction rates for in-situ purging experiments, zero-, first-, and second-order reaction kinetics were studied. Assuming irreversible reactions, reaction expressions are as follows (Equation 3-6 through Equation 3-8):

\[
\text{Zero-order: } \frac{dC}{dt} = -k 
\]

\[
\text{First-order: } \frac{dC}{dt} = -kC 
\]

\[
\text{Second-order: } \frac{dC}{dt} = -kC^2 
\]

where \(C\) is the concentration of total Hg in solution, \(k\) is the apparent kinetic rate constant, and \(t\) is the reaction time. The above expressions were integrated from \(t=0\) to \(t=t\) (Equation 3-9 through Equation 3-11):

\[
\text{Zero-order: } C_t = C_0 - kt 
\]

\[
\text{First-order: } C_t = C_0 e^{-kt} 
\]

\[
\text{Second-order: } \frac{1}{C_t} = \frac{1}{C_0} + kt 
\]

where \(C_0\) is the initial concentration and \(C_t\) is the concentration at reaction time \(t\) of total Hg in solution. Regression analysis for the loss of Hg from solution with purge and UV irradiation over time was conducted. All reported rate constants were obtained from linear least squares analysis of the experimental data (regressing \([C]\) versus time for zero order reactions, and \(\ln [C]\) versus time for first order reactions, where \(C\) equals the molar concentration of Hg).
CHAPTER 4
CHARACTERIZATION OF SILICA-TITANIA COMPOSITES

Introduction

In this chapter, a range of TiO₂ masses were immobilized in porous silica-gels using an acid catalyzed sol-gel process.¹⁵ Unlike many SiO₂/TiO₂ composites discussed in the literature, the material in this work was prepared by adding commercially available TiO₂ particles (DP25) into the liquid sol before gelation. Pore diameter was also altered during the synthesis by varying the HF concentration added to the liquid sol. The combined material is herein referred to as a silica-titania composite (STC). This material has been studied for use in a variety of photocatalytic applications such as Hg removal from flue gas,¹⁴,¹⁵ Hg recovery from caustic exhaust emitted from the chlor-alkali industry,¹⁶ and the degradation of volatile organic compounds in gas emitted from pulp and paper mills.¹⁷ While optimal material conformations were found for the applications listed, it was not well understood how the material characteristics changed with HF concentration and TiO₂ loading. Knowledge of the STC properties is integral to understanding the use of STC for treatment of both organic and inorganic contaminants.

The following discusses the composite characteristics as a function of HF concentration and TiO₂ loading of the STC. Physical features were analyzed using secondary electron imaging and surface area analysis. Surface charge behavior for the STCs and TiO₂ characteristics such as particle size, band gap and available TiO₂ surface area of the composite were determined.

Results

SEM

SEM images provide evidence of surface texture and primary particle size distribution for various STC compositions. The two parameters explored in the present work were HF concentration and TiO₂ loading. It was expected that both parameters would have an impact on
the surface morphology. Since HF catalyzes the sol-gel formation, it was necessary to assess its impact on the silica particle size in the composite photocatalyst. As shown in images A, B, and C in Figure 4-1, as the concentration of HF was increased the surface particle size appears to decrease. This may be the result of shorter gelation times for higher concentrations of HF, which resulted in a shorter period for particle growth and therefore a smaller particle size. With respect to TiO\textsubscript{2} mass loading, the particle size appears not affected as the titanium dioxide loading increased from 12 to 70\%\textsubscript{wt} as shown in images C and D in Figure 4-1. While weight percentage of TiO\textsubscript{2} largely increased, there is little visible change in the particle morphology.

![SEM images (A: STC-0.25-12, B: STC-1-12, C: STC-2-12, D: STC-2-70)(SEI, 5.0 kV, X50,000 , WD 8 mm).](image)

**Adsorption-Desorption Isotherms**

Adsorption-desorption isotherms for each of the STCs are shown in Figure 4-2. The isotherms are Type IV and display H1 and H2 hysteresis loops (as defined by the IUPAC characteristic of mesoporous materials). The silica/STC-0.25 materials are defined by H2 hysteresis while the silica/STC-1 and silica/STC-2 materials are H1. Type H1 hysteresis is indicative of materials of uniform spheroid particles that tends to be monoporous or possess a
Figure 4-2. Calcined STC nitrogen adsorption-desorption isotherms a) silica/STC-0.25, b) silica/STC-1, and c) silica/STC-2 as measured with a Quantichrome AutoSorb
narrow pore size range. This was a confirmed characteristic of the silica/STC-1 and silica/STC-2 materials by the presence of approximately uniform spheroid particles shown by the SEM images in Figure 4-1. While silica/STC-0.25 materials also possesses spheroid particles, but of larger size, H2 hysteresis suggests a more complex pore structure exists for this material. As spheroid particles grow larger, pores become less cylindrical and more undefined which could result in a change in hysteresis shape. Type H2 hysteresis is generally associated with ink bottle pores (narrow necks and wide bodies) with an extensive pore network.\textsuperscript{133} Smaller pore sizes which connect larger more interior pores to the surface would result in a delayed desorption curve until relative pressures low enough for the small pores to empty, such as was exhibited in silica/STC-0.25 isotherms. Poorly defined pore shape or distribution in a disordered material, which results in pore blocking and percolation, could also cause the H2 loop.\textsuperscript{133}

Although the silica/STC-0.25 materials exhibit H2 hysteresis loops, the STC-0.25-70 isotherm returned to a more H1 shape. The STC-0.25-70 hysteresis loop narrows at a relative pressure of about 0.8, rather than 0.5 to 0.6 for the silica-0.25, STC-0.25-12, and STC-0.25-30. This suggests that the 70 \%wt TiO\textsubscript{2} loading may increase the size of the pore neck, allowing the pore body to empty at higher relative pressures, or result in a less extensive pore network, as evidenced by the decrease in total pore volume.

The above isotherms were analyzed to produce BET surface area, average pore diameter and total pore volume data, which are summarized in Table 3. DP25, not illustrated, has a measured surface area of 49.2 m\textsuperscript{2}/g in this work. Both HF concentration and TiO\textsubscript{2} loading influenced the total pore volume and surface area of the composites. HF is known to cause widening of silica gel pores;\textsuperscript{94} thus, as HF increased, pore volume increased and surface area
decreased. The addition of the non-porous TiO₂ to the porous silica gel resulted in an overall decrease in specific surface area and pore volume.

Table 4-1. BET specific surface area, pore diameter and pore volume values for calcined STC as measured by nitrogen adsorption/desorption (AutoSorb)

<table>
<thead>
<tr>
<th></th>
<th>BET surface area (m²/g)</th>
<th>Average Pore Diameter (Å)</th>
<th>Pore Volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>silica-0.25</td>
<td>630 ±15</td>
<td>58.0 ±0.6</td>
<td>0.910 ±0.03</td>
</tr>
<tr>
<td>STC-0.25-12</td>
<td>594 ±15</td>
<td>50.6 ±0.5</td>
<td>0.767 ±0.03</td>
</tr>
<tr>
<td>STC-0.25-30</td>
<td>560 ±14</td>
<td>46.0 ±0.5</td>
<td>0.647 ±0.02</td>
</tr>
<tr>
<td>STC-0.25-70</td>
<td>326 ±8</td>
<td>71.6 ±0.7</td>
<td>0.584 ±0.02</td>
</tr>
<tr>
<td>silica-1</td>
<td>430 ±11</td>
<td>122 ±1.2</td>
<td>1.31 ±0.04</td>
</tr>
<tr>
<td>STC-1-12</td>
<td>396 ±10</td>
<td>113 ±1.1</td>
<td>1.19 ±0.04</td>
</tr>
<tr>
<td>STC-1-30</td>
<td>269 ±7</td>
<td>135 ±1.3</td>
<td>0.903 ±0.03</td>
</tr>
<tr>
<td>STC-1-70</td>
<td>273 ±7</td>
<td>101 ±1.0</td>
<td>0.690 ±0.02</td>
</tr>
<tr>
<td>silica-2</td>
<td>282 ±7</td>
<td>239 ±2.3</td>
<td>1.68 ±0.06</td>
</tr>
<tr>
<td>STC-2-12</td>
<td>230 ±6</td>
<td>253 ±2.5</td>
<td>1.46 ±0.05</td>
</tr>
<tr>
<td>STC-2-30</td>
<td>203 ±5</td>
<td>228 ±2.2</td>
<td>1.15 ±0.04</td>
</tr>
<tr>
<td>STC-2-70</td>
<td>167 ±4</td>
<td>167 ±1.6</td>
<td>0.696 ±0.02</td>
</tr>
</tbody>
</table>

To understand if the surface area and pore volume changes were due to the addition of non-porous TiO₂ to a porous silica gel or by TiO₂ blocking silica gel pores, theoretical surface areas were calculated. For each STC, the surface area data for TiO₂ (49.2 m²/g) was multiplied by its mass fraction of the STC to determine its maximum surface area contribution to the STC. This value was added to the remaining mass fraction multiplied by the surface area of the STC with the same acid ratio and a 0%wt TiO₂ loading to obtain the theoretical surface area of the STC. These values are compared to the measured surface area values (Table 3) in Figure 4-3. The solid diagonal line in the figure represents where the theoretical surface area would be equal to the measured surface area. Measured surface area values are generally reproducible within 5%, which is indicated by the dashed diagonal lines above and below the solid diagonal line. These lines are for visual reference. In general, the theoretical surface areas are equal to or slightly lower than the corresponding measured value. Thus, there is a higher degree of porosity
than expected for some of the STC. This data does not suggest that significant pore blockage occurred as a result of TiO₂ addition and supports that the composite is well defined by its components.

Figure 4-3. Comparison of theoretical values for surface area versus actual measured values.

Additionally, adsorption-desorption isotherms were measured using an alternate set of prepared STC that had not been calcined. The BET characterization of this media is presented in Table 4-2. These materials were subsequently used for Hg testing which results are presented in the following chapter. Calcination was not completed because the washing was assumed to reach sufficiently low fluoride and TOC levels (i.e., less than 1 mg/L concentrations as seen after the washing of STC pellets) as not to impact Hg testing. Additionally, with the thought of future commercialization potential, it would be advantageous to avoid the energy consumptive set of heat treatment. While differences exist between Table 4-1 and 4-2, these are mostly for the smaller pore diameter materials. The AutoSorb technology uses a more sensitive detector for gas pressure than that of the NOVA which would account for the differences. Despite slightly different number values, very similar trends exist for the washed STC in comparison with
calcined samples analyzed on the Autosorb. Additionally, the isotherms for the washed STC carry the same characteristic shapes and hysteresis loops as that of the calcined STC (Figure 4-4). Therefore, it was evident that the pore structure was unchanged by calcination at 450 °C and that the investigated characteristics for the calcined STC would apply to that of the washed STC.

Table 4-2. BET specific surface area, pore diameter and pore volume values for washed STC as measured by nitrogen adsorption/desorption (NOVA)

<table>
<thead>
<tr>
<th>Material</th>
<th>BET Surface Area m²/g</th>
<th>Average Pore Diameter Å</th>
<th>Pore Volume cc/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>silica-0.25</td>
<td>764 ± 19</td>
<td>33 ± 0.1</td>
<td>0.634 ± 0.03</td>
</tr>
<tr>
<td>STC-0.25-12</td>
<td>796 ± 20</td>
<td>33 ± 0.1</td>
<td>0.654 ± 0.03</td>
</tr>
<tr>
<td>STC-0.25-30</td>
<td>655 ± 16</td>
<td>36 ± 0.1</td>
<td>0.591 ± 0.03</td>
</tr>
<tr>
<td>STC-0.25-60</td>
<td>441 ± 11</td>
<td>46 ± 0.1</td>
<td>0.506 ± 0.03</td>
</tr>
<tr>
<td>silica-1</td>
<td>467 ± 12</td>
<td>116 ± 0.1</td>
<td>1.351 ± 0.07</td>
</tr>
<tr>
<td>STC-1-12</td>
<td>398 ± 10</td>
<td>101 ± 0.1</td>
<td>1.008 ± 0.05</td>
</tr>
<tr>
<td>STC-1-30</td>
<td>358 ± 9</td>
<td>112 ± 0.1</td>
<td>1.006 ± 0.05</td>
</tr>
<tr>
<td>STC-1-60</td>
<td>271 ± 7</td>
<td>107 ± 0.1</td>
<td>0.725 ± 0.04</td>
</tr>
<tr>
<td>silica-2</td>
<td>236 ± 6</td>
<td>265 ± 0.3</td>
<td>1.565 ± 0.08</td>
</tr>
<tr>
<td>STC-2-12</td>
<td>223 ± 6</td>
<td>250 ± 0.3</td>
<td>1.397 ± 0.07</td>
</tr>
<tr>
<td>STC-2-30</td>
<td>192 ± 5</td>
<td>244 ± 0.2</td>
<td>1.176 ± 0.06</td>
</tr>
<tr>
<td>STC-2-60</td>
<td>200 ± 5</td>
<td>169 ± 0.2</td>
<td>0.843 ± 0.04</td>
</tr>
</tbody>
</table>

Also utilizing the NOVA instrumentation, the BET surface area values for the produced titania material are compared to that of DP25 in Table 4-3. A higher surface area was not realized for the SA(450) sample. While TPT(450) and QHZ(450) materials demonstrated an increased surface area, it was by a small degree. Sample QHZ did however show a very high surface area, but this material was not calcined so was predicted to be amorphous instead of crystalline. STC materials prepared for optimization testing for Hg removal were also analyzed (Table 4-4). A very large pore diameter was realized with the STC-4-60 sample while maintaining a high pore volume. STC-2-60QHZ appeared to have similar characteristics to that of STC-2-60.
Figure 4-4. STC nitrogen adsorption-desorption isotherms a) silica/STC-0.25, b) silica/STC-1, and c) silica/STC-2 as measured with a Quantichrome NOVA
Table 4-3. BET specific surface area, pore diameter and pore volume values for TiO₂ materials used in STC production as measured by nitrogen adsorption/desorption (NOVA)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti Precursor</th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP25</td>
<td>proprietary</td>
<td>50 ± 1</td>
</tr>
<tr>
<td>SA(450)</td>
<td>Ti(OCH(CH₃)₂)₄</td>
<td>42 ± 1</td>
</tr>
<tr>
<td>TPT(450)</td>
<td>Ti(OC₃H₂)₄</td>
<td>92 ± 2</td>
</tr>
<tr>
<td>QHZ(450)</td>
<td>TiCl₄</td>
<td>68 ± 2</td>
</tr>
<tr>
<td>QHZ</td>
<td>TiCl₄</td>
<td>332 ± 8</td>
</tr>
</tbody>
</table>

Table 4-4. BET specific surface area, pore diameter and pore volume values for washed STC produced to test for material optimization as measured by nitrogen adsorption/desorption (NOVA)

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface Area m²/g</th>
<th>Average Pore Diameter Å</th>
<th>Pore Volume cc/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>STC-2-70</td>
<td>320 ± 9</td>
<td>142 ± 0.2</td>
<td>0.987 ± 0.05</td>
</tr>
<tr>
<td>STC-4-60</td>
<td>110 ± 3</td>
<td>333 ± 0.3</td>
<td>0.916 ± 0.05</td>
</tr>
<tr>
<td>STC-2-60QHZ</td>
<td>179 ± 4</td>
<td>170 ± 0.2</td>
<td>0.758 ± 0.04</td>
</tr>
</tbody>
</table>

**Isoelectric Point**

Four different silica/STCs, silica-0.25, STC-0.25-70, silica-2, and STC-2-70, were analyzed with streaming potential to elucidate the effect of HF concentration and TiO₂ loading on IEP. The selected materials represent the minimum and maximum quantities of HF and TiO₂. The results of the analyses are presented in Table 4-5.

Table 4-5. IEP Values

<table>
<thead>
<tr>
<th></th>
<th>IEP</th>
</tr>
</thead>
<tbody>
<tr>
<td>silica-0.25</td>
<td>2.79 ±0.15</td>
</tr>
<tr>
<td>STC-0.25-70</td>
<td>3.19 ±0.17</td>
</tr>
<tr>
<td>silica-2</td>
<td>2.85 ±0.15</td>
</tr>
<tr>
<td>STC-2-70</td>
<td>2.94 ±0.15</td>
</tr>
</tbody>
</table>

The IEP of DP25 has been measured to be 6.8. Silica gels generally possess an IEP around 2. The results in Table 6 range from 2.79 to 3.19 for the STCs tested, indicating that silica functional groups dominate the surface of all the STCs. The IEP was not sensitive to the
quantity of HF or TiO₂ in the range used in STC synthesis for this research. Therefore, STCs can be tailored without largely effecting electrostatic interactions.

**X-Ray Diffraction**

Using the Scherrer equation (Equation 3-3), particle size (t) can be estimated. Full peak width (B) at half maximum corrected for instrumental broadening was determined to be 0.004800, 0.005007, and 0.005200 radian for DP25, STC-0.25-12, and STC-2-12 (Figure 4-5). From this, particle sizes for each of the three listed samples were calculated.

![XRD pattern](image)

Figure 4-5. Effect of synthesis procedure on XRD pattern, from top DP25 TiO₂, STC-0.25-12, STC-2-12.

Using the analysis described in the Chapter 3, the Scherrer equation indicates that particle sizes for the DP25 anatase crystalline phase decreased slightly from 30.0 for DP25 to 28.7 and 28.5 nm in the STCs. Despite the change in HF concentration, TiO₂ particle size seems to remain the same. The somewhat smaller particle size in the composite material may be due to an increase in solubility of Ti during the synthesis process due to the presence of hydrofluoric and nitric acid. Since the decrease in particle size estimate was 5% or less, this was not believed to
have a significant adverse impact on photocatalytic activity; however it could potentially have an
effect on photocatalytic activity if the acid concentration is increased dramatically.

**Diffuse Reflectance**

Diffuse reflectance measurements were used to estimate bandgap energies for the various
STC formulations. Figure 4-6 shows the results of the least squares regression for determination
of the Kubelka-Munk parameter (Equation 3-2). The corresponding bandgap energies were
found to be 3.15, 3.17, 3.15, and 3.21 eV for STC-0.25-12, STC-1-12, STC-2-12, and DP25
respectively. These values indicate that there was a slight decrease in the estimated bandgap
energy for STCs as compared to DP25 alone due to composite synthesis procedures. The
difference is minimal however and still corresponds to light of wavelengths less than 400 nm
necessary for inducing photocatalytic redox reactions, which is the same as for unprocessed
DP25.

Figure 4-6. Diffuse reflectance spectra of DP25 TiO$_2$, STC-0.25-12, STC-2-12 using the
Kubelka-Munk Parameter.
**TiO₂ Surface Analysis**

Understanding the specific surface area of TiO₂ in a composite material is extremely important to properly assess the photocatalytic capability of the material. Many times, composite materials will be compared to their photocatalytic counterpart on a mass basis. But this comparison lacks specific surface area details. For this reason, Marugan et al. modified a functionalization procedure developed by Mutin et al. to determine the available surface area of TiO₂ in SiO₂/TiO₂ composite materials.

To begin, the procedure was tested with a variety of STC to ensure that the methodology was well suited to the materials produced for this work. A smaller pore diameter and TiO₂ loading material (STC-0.25-7) and a larger pore diameter and TiO₂ loading material (STC-2-50) were tested for impact of time of functionalization and effect of calcination at 450 °C. The resulting TiO₂ surface area data can be seen in Figure 4-7.

![Figure 4-7. Comparison of phosphorous functionalization time for TiO₂ surface area analysis](image)

Indeed, as TiO₂ loading in the STCs increased, so did the available TiO₂ surface area. The impact of functionalization time did not significantly alter the value for TiO₂ surface area/g STC.
for either pore diameter materials. The functionalization time of 24 hours was determined to be sufficient for pseudo equilibrium conditions. Additionally, there was little impact on the functionalization of TiO₂ based on whether the material had been calcined or not. This was hypothesized since crystallinity and therefore density of surface functional groups of DP25 should not be impacted at this temperature and a change in mass due to volatilization of organic material should not be significant in comparison to the total mass of the functionalized sample.

Testing proceeded with the calcined array of STC listed in Table 4-1 using a one day functionalization period. Figure 4-8 illustrates the measured surface area values of available m² TiO₂ per gram of media as shown by the bar values. Silica was tested to ensure that functionalization of its surface groups by phosphorous did not occur and that only Ti surface groups were responsible for the phosphorous contribution. Very small values of phosphorous were detected but were attributed to residual remaining from the rinsing step of the procedure. As seen below, a positive correlation between the measured TiO₂ surface area and TiO₂ loading can be identified in Figure 4-8.

Figure 4-8. Available TiO₂ surface area for various calcined silica and STC measured by phosphorous functionalization (x = HF:HNO₃ during STC synthesis)
Despite the positive correlation, the measured TiO₂ surface area is less than the total surface area of TiO₂ added during the synthesis of the STC. This reduction in available TiO₂ surface area is expected since surface area can be reduced by adherence onto the composite surface or encapsulation within the composite. In addition, loss of TiO₂ particles could occur during the synthesis, grinding, and sieving procedures, thereby resulting in a decrease in TiO₂ surface area. ICP analysis of total Ti concentration was used to determine that less than 8%wt of TiO₂ was lost due to these procedures. Table 7 compares the TiO₂ surface area with these losses taken into consideration. The synthesis method data represents the total TiO₂ surface area added to the STC. This value was calculated from the surface area of DP25 (50 m²/g) and the mass percent of TiO₂ added to the composite during synthesis. The digestion procedure data represents the total TiO₂ surface area after processing losses of TiO₂. Here, the mass percentage of TiO₂ in the composite was calculated by digestion of the STC and ICP analysis for Ti to determine the mass of TiO₂. This value was multiplied by the surface area of DP25 to determine the surface area of TiO₂ per mass of STC. Lastly, the functionalization procedure data corresponds to the measured TiO₂ surface area as determined by the Marugan et al.¹²⁷ functionalization procedure. Comparing the digestion procedure data to the functionalization procedure data, the percent of inaccessible TiO₂ surface area was calculated. This value represents the TiO₂ surface area lost to adherence and encapsulation. While significant amounts of TiO₂ surface area can be lost within the silica structure, up to 87% of the TiO₂ in the composite can be available on the surface.

Also interesting was the difference in available TiO₂ surface area with the difference in HF concentration. At 12 and 30 %wt TiO₂ loadings, STC-0.25 had a greater loss of available TiO₂ surface area than STC-1 and STC-2. While a greater loss is expected for adherence of TiO₂
particles with STC-0.25, since it has the highest composite surface area, this loss should be small
due to the size of the TiO₂ nanoparticles. Therefore, the loss of available TiO₂ surface area
should be primarily due to TiO₂ particles that were encapsulated. This theory supports the
change in hysteresis shape and therefore pore structure for STC-0.25 materials (Figure 4-2). In
addition, encapsulated TiO₂ could increase porosity by acting as filler in the silica network so the
pore structure could extend further, which would explain why measured surface areas are greater
than expected (Figure 4-3). Another option would be the accessibility of the STC-0.25 pores to
the phenylphosphonic acid molecule. This molecule (dimensions of approximately 11 by 8 by
16 Å₁²₈,₁₂₉) might not be able to move through the bottle neck of the smallest pore diameters to
reach TiO₂ sites and therefore those sites would be determined inaccessible.

More dramatically, 70 %wt TiO₂ loadings exhibit the highest loss of available TiO₂ surface
area as concentration of HF is reduced. With such a high loading of TiO₂, encapsulation of the
material into the composite becomes more difficult for the smaller pore size STCs. A change in
pore structure may have occurred as was evidenced by the long tail of the hysteresis loops for
STC-0.25-70 and STC-1-70 isotherms.

Table 4-6: Calculated versus measured TiO₂ surface areas of calcined STC

<table>
<thead>
<tr>
<th></th>
<th>TiO₂ surface area (m²/g STC)</th>
<th>% inaccessible TiO₂ surface area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>synthesis method</td>
<td>digestion procedure procedure</td>
</tr>
<tr>
<td>STC-0.25-12</td>
<td>5.93 ±0.15</td>
<td>4.99 ±0.13</td>
</tr>
<tr>
<td>STC-0.25-30</td>
<td>14.4 ±0.35</td>
<td>12.9 ±0.86</td>
</tr>
<tr>
<td>STC-0.25-70</td>
<td>32.7 ±0.80</td>
<td>30.5 ± 1.28</td>
</tr>
<tr>
<td>STC-1-12</td>
<td>6.18 ±0.15</td>
<td>5.12 ±0.46</td>
</tr>
<tr>
<td>STC-1-30</td>
<td>14.8 ±0.36</td>
<td>13.2 ±0.25</td>
</tr>
<tr>
<td>STC-1-70</td>
<td>34.4 ±0.84</td>
<td>30.8 ±0.04</td>
</tr>
<tr>
<td>STC-2-12</td>
<td>6.22 ±0.15</td>
<td>4.81 ±0.60</td>
</tr>
<tr>
<td>STC-2-30</td>
<td>15.2 ±0.37</td>
<td>14.2 ±1.29</td>
</tr>
<tr>
<td>STC-2-70</td>
<td>31.6 ±0.84</td>
<td>30.0 ±1.35</td>
</tr>
</tbody>
</table>
Also calculated was the percentage of TiO₂ on the total surface area of the STCs using the digestion procedure specific surface area ($m^2$ TiO₂ /g STC from Table 7) divided by the corresponding BET specific surface area ($m^2$/g) (Table 4-1). While the weight percent of TiO₂ in the composite significantly increases and much of it is available, the surface area percent of TiO₂ on the STC ranges from only 0.6 to 14% at the maximum (for STC-0.25-12 and STC-2-70) (Figure 4-9).

![Figure 4-9. Comparison of TiO₂ available surface area for various calcined STC versus mass loading of TiO₂ in STC](image)

This means that silica represents 84 to 99.4% (for STC-0.25-12 and STC-2-70) of the STC surface since silica has such a high specific surface area compared to TiO₂. The low surface area percent of TiO₂ agrees with the low IEP data determined by streaming potential. The IEP is dependent upon the surface functional groups of the materials. Although silica and titania have a similar number of hydroxyl groups per surface area, the silica functional groups will dominate the electrostatics since the silica surface area dominates.

The functionalization procedure was also carried out on the 12% wt and 60% wt TiO₂ STC listed in Table 4-2. The resulting available TiO₂ surface area and TiO₂ weight contribution are
presented in Figure 4-10. The available TiO₂ surface areas carry a similar trend to that of the calcined STC in Figure 4-8 with STC-0.25-12 and STC-2-60 having higher available TiO₂ surface areas than anticipated. Since each STC batch is prepared individually, the material properties will be dependent upon strict synthesis conditions.

![Figure 4-10. Available TiO₂ surface area for various STC used in Hg experiments measured by phosphorous functionalization](image)

In an attempt to improve the surface area and/or functionality of TiO₂ immobilized in the silica macrosupport, various TiO₂ production methods were carried out and the resulting media was analyzed with the phenylphosphonic acid functionalization procedure. The analysis of the collected data was slightly altered to compare the newly produced titania materials to that of DP25. Figure 4-11 illustrates the molar ratio of phosphorous atoms on the surface of the newly produced material to phosphorous atoms on DP25 after functionalization. Since phosphorous associates with titanol groups, the moles of phosphorous found would be directly related to the quantity of surface functional groups. Values over 1 meant that the newly produced material had more surface groups available to react with phosphorous per mass than that of DP25. A greater number of surface groups could be the result of either a greater density of groups and/or a greater
surface area. Using the surface area data from Table 4-3, the quantity of phosphorous functionalized to the surface of the materials was divided by the surface area to determine the µmol of phosphorous per m² of material (Figure 4-12). A very similar quantity resulted for all of the materials indicating that the number of functional groups per surface area was not increased from that of DP25.

![Figure 4-11. Comparison of µmoles of phosphorous functionalized per mass of material and mass contribution of Ti for each material (secondary y-axis)](image)

Also shown in Figure 4-11 and Figure 4-12 is a red line representing the mass contribution of Ti to the material (secondary y-axis). While DP25, SA(450), TPT(450) and QHZ(450) possessed very similar mass contributions of Ti, QHZ demonstrated a lower value. Since QHZ was not calcined, it is hypothesized to be an amorphous material with some mass contributions that the other materials lost during calcination.

Based off of these predictions, QHZ was the most promising TiO₂ material to enhance Hg removal based on its greater surface area per mass and similar quantity of functional groups per surface area and therefore higher surface functionality per mass which could lead to greater Hg adsorption.
Due to the promising nature of QHZ, the material was immobilized in the silica macrosupport to produce STC-2-70QHZ. This and other optimization formulas were compared using the phenylphosphonic acid functionalization procedure. Since all of the composite materials were not produced with the same TiO$_2$ precursor, the bar values represent the µmol of phosphorous functionalized to titanol groups per mass of media. The line value represents the mass contributions of Ti per mass of media (Figure 4-13).

The goal of optimization was to increase the quantity of TiO$_2$ surface groups for enhanced Hg removal above that of STC-2-60. From comparing the bar values, only small differences in the quantity of available Ti groups exist between the different STC formulations. In agreement from above, the STC with QHZ has a lower mass contribution of Ti. Unfortunately, the significantly greater surface area per mass for the QHZ material did not translate into a greater number of available Ti surface sites in the STC. As a verification, these materials were later tested for their Hg capacities.
In summary, STC-2-60 reached the maximum Hg removal under the conditions studied. STC-2-60, while slightly outperforming TiO$_2$, would require much less filtration requirements to separate the solid from the liquid stream and would be advantageous over using TiO$_2$ alone.
CHAPTER 5
TRACE LEVEL AQUEOUS MERCURY REMOVAL USING SILICA-TITANIA COMPOSITES

Introduction

A promising treatment method for aqueous Hg removal is semiconductor photocatalysis on TiO$_2$.\textsuperscript{41,79,82,136} In these studies, Hg removal was achieved through the reduction of divalent Hg species to Hg$^0$ via reactions with the photogenerated TiO$_2$ electrons. Over 95% Hg removal could be achieved beginning with initial concentrations of 100 mg/L of Hg. However, Hg removal at trace levels, ca. 100 µg/L Hg, was not studied. Considering current Hg regulations and health concerns, the occurrence of mg/L Hg waste streams are rare and sub 10 µg/L Hg concentrations are desired in the environment. Such low levels are currently enforced in the Great Lakes region.\textsuperscript{9} Therefore, to address present day and future Hg management needs, this work evaluates the potential for silica-titania composites to remove trace level Hg from aqueous solutions.

Mercury Removal: Hg(NO$_3$)$_2$

Pseudo Equilibrium Adsorption

The impact of media loading on the removal of Hg from 100 µg/L aqueous solutions by adsorption onto STC-0.25-12 was compared with that of its parent compounds, DP25 TiO$_2$ and silica-0.25 after reaching pseudo equilibrium conditions (Figure 5-1). A mass loading of 1 g/L was selected for further testing as this was the point where TiO$_2$ and STC Hg removal per mass begins to diverge. Additionally, this concentration has been used previously in TiO$_2$ testing for optimal light distribution and minimal agglomeration. This value has also been used in other photocatalystic studies as an optimal TiO$_2$ dosage for light distribution and reduced agglomeration for greater availability of reaction sites.\textsuperscript{54,137} As TiO$_2$ loadings increased over 1 g/L, Hg removal decreased, indicating that particles were agglomerating and there was a loss of
adsorption sites. The reverse is true for silica-0.25 which had increased removal with increased mass. Since the silica and STCs are much larger in primary particle size, agglomeration is not likely for the silica particles. Thus as mass loading increased, so did the number of adsorption sites. Interestingly, Hg removal seemed to reach a maximum for STC-0.25-12 at 0.5 g/L media loadings.

Figure 5-1. Effect of mass loading on pseudo equilibrium for 100 µg/L Hg removal for 24 hours.

**Adsorption**

Adsorption onto STC-0.25-12, DP25 TiO₂ and silica-0.25 was then studied in the batch reactor for the removal of Hg from 100 µg/L aqueous solutions. Equal mass loadings, 1 g media/L solution as selected through pseudo equilibrium studies, of each material were used for the comparison. STC-0.25-12 was selected with the thought of commercialization in mind. This formulation contains the smallest volume of HF and TiO₂ and would therefore be the least expensive STC to produce. Under adsorption alone (Figure 5-2a), silica does not have a large affinity for Hg. However, once TiO₂ is added to create a STC, Hg removal sharply increased. STC-0.25-12 performed very similarly to the benchmark DP25 TiO₂. The Hg
Figure 5-2. 100 µg/L Hg removal a) adsorption alone (Ads), b) UV photocatalysis (UV) and c) adsorption in the dark at elevated temperatures (Ads+heat) onto silica-0.25, STC-0.25-12, and DP25 TiO₂.
concentration is significantly lowered within only 5 minutes and additional adsorption continued slowly up to 60 minutes which is where pseudo equilibrium was determined to be achieved. These results indicated that STC are a very promising sorbent for Hg removal.

**Photocatalysis**

It was expected, based on previous literature researching higher concentrations of Hg\(^{41,76,79,80,82}\), that Hg removal under photocatalysis conditions involving TiO\(_2\) would be even greater than adsorption alone. Once irradiated with UV, the TiO\(_2\) and STC system performed unexpectedly since an increase in removal was expected (Figure 5-2b). The silica-0.25 did however perform as anticipated; its Hg removal did not deviate from adsorption alone conditions since it did not contain any photocatalytic materials. While further Hg removal via TiO\(_2\) photocatalysis in the presence of UV was predicted, Hg removal improved only marginally. Even more surprisingly, the performance of STC-0.25-12, which had performed as well as TiO\(_2\) under adsorption alone, was retarded under UV irradiation until greater contact times (60 minutes).

**Comparison**

To determine the cause of the unexpected results, the differences between the adsorption alone system and the photocatalysis system were scrutinized. Besides the addition of UV irradiation to the photocatalysis system, an increased solution temperature over the contact time had occurred due to the direct contact of the UV bulb with the Hg solution. Therefore, the effect of increased solution temperature on Hg removal was investigated. Adsorption experiments with the same temperature profile as that of the photocatalysis experiments were performed to isolate the effects of temperature change. The heat profile was achieved using the adsorption set-up on a heated stir plate to increase the temperature slowly over time (an increase of about 30 °C over
60 minutes). As an example, the average temperature profiles for each reactor condition employing STC-0.25-12 are plotted in Figure 5-3.

Figure 5-3. Average temperature profiles for experimental conditions employing STC-0.25-12

STC-0.25-12 and TiO₂, in the absence of UV but with an elevated solution temperature to mimic the temperature of the solution in the presence of UV, performed very similarly to each other (Figure 5-2c) and to that of the original adsorption alone results. Silica-0.25 was minimally impacted by the change in conditions. To further elude the differences between experimental conditions, the results were graphed based on sorbent (Figure 5-4). As was previously noted, Hg removal by Silica-0.25 remained unchanged as experimental conditions changed (Figure 5-4c). TiO₂ exhibited a slight improvement in Hg removal under 60 minutes for the UV and adsorption at elevated temperatures compared to adsorption alone. However, once 60 minutes is reached, the same Hg removal is attained. Therefore, the effect of added heat to the system is an increased rate of Hg removal. Photochemical reactions are ineffective for Hg removal beyond that of adsorption alone at these trace concentrations.
Figure 5-4. 100 µg/L Hg removal onto a) silica-0.25, b) DP25 TiO₂, and c) STC-0.25-12 via adsorption alone (Ads), adsorption in the dark at elevated temperatures (Ads+heat) and UV photocatalysis (UV).
On the contrary to the results for Silica-0.25 and TiO₂, it can be confirmed that Hg removal under UV irradiation is distinctively less than that by adsorption and adsorption with elevated temperatures (Figure 5-4b) until 60 minutes is reached. Here it is evident that the negative change in Hg removal by STC-0.25-12 under photocatalysis experimental conditions is caused by UV irradiation alone and not a change in temperature.

**Effect of UV on TiO₂**

While STC-0.25-12 exhibited a delay in Hg removal in the presence of UV irradiation as compared to in the dark, this phenomena was not seen with the individual Silica-0.25 or TiO₂ materials. Under 254 nm UV light, TiO₂ will be photoactive and generate e⁻/h⁺ pairs. Hg removal by TiO₂ in this work was not affected by the presence (photocatalysis system), or absence (adsorption with heat) of these processes. The affinity of Hg for silica was also unchanged as silica is not reactive under the presence of UV. Therefore, the effect of UV on the adsorbate was considered to be the significant factor causing a reduced Hg removal at times under 30 minutes.

**Effect of UV on Hg**

Photochemical reactions of Hg due to the presence of sunlight have been gaining attention as of late. Therefore, it was desirable to investigate the effect of Hg speciation under UV illumination without a photocatalyst to further isolate the changes responsible for a decreased Hg removal for shorter contact times in the UV STC system. For these studies, the same batch reactor was used without media. Hg solutions were exposed to UV and a simultaneous nitrogen gas purge through the purge tube. The nitrogen flow was controlled to 2 L/min and a glass frit was installed on the end of the purge tube to decrease gas bubble size. Nitrogen was selected for this application to be an inert gas that would not interact with Hg or contribute to any redox reactions in the presence of UV. A control study without UV was performed to ensure that there
was no Hg loss due to purging alone. Another control with UV but no purge was also performed to ensure there was no Hg loss due to UV without a purge. The results in Figure 5-5 show that the controls, with either a purge or UV, did not remove appreciable quantities of Hg in agreement with high level Hg photocatalysis experiments. However, in the presence of both the purge and UV irradiation, Hg concentrations diminished substantially. Trace level aqueous divalent Hg (the dominant species in an aqueous solution of Hg(NO₃)₂ as seen in Figure 2-1) could indeed be reduced to elemental Hg in the presence of UV and be volatilized into the nitrogen stream and removed from solution. As further verification that volatilization occurred, no filterable species of Hg greater than 0.45 µm were found.

Figure 5-5. Hg reduction in the presence of UV (254 nm) and removal by 2 L/min/100 mL nitrogen purge through a glass frit

Since elemental Hg can be produced by photochemical reactions in the absence of TiO₂, the speciation change will occur in all solutions irradiated by UV light even before contacting the photocatalyst. As an additional test, a Hg solution was irradiated with UV followed by an immediate nitrogen purge once the light was extinguished. This resulted in little to no Hg removal from solution. Although Hg can be reduced by photochemical reactions, it can also be
oxidized very quickly once the UV lamp is extinguished. Therefore, both reduction, via UV, and oxidation, in the absence of UV photons, of Hg occur in solution. TiO$_2$, being of nanosize and a photocatalyst, will absorb UV and likely decrease the reduction reactions of Hg in solution promoting more oxidized Hg in solution. It is inconclusive what valence Hg finally binds to the surface of the TiO$_2$, but only that UV does not reduce the capacity of Hg for TiO$_2$ alone. In addition, due to its size (30 nm particles that cluster to greater than 45 nm), TiO$_2$ will have more interactions with Hg, which can lead to faster adsorption, over much larger 45 – 90 micron particles during a given contact time. Due to these properties, the removal of Hg by TiO$_2$ is not impacted by the presence or absence of UV light at low concentration of Hg. The removal of Hg by STC-0.25-12, with a larger particle size than TiO$_2$ and a lower photocatalyst (TiO$_2$) surface area, is negatively impacted by the presence of elemental Hg.

**Effect of Primary Particle Size**

Since Hg removal by nanosized TiO$_2$ was not impacted by UV but larger micron sized STC was, the importance of particle size was investigated. As stated in the Material and Methods section, STC-0.25-12 was ground and wash sieved to a 45 – 90 µm size fraction. The fraction less than 45 µm was wash filtered to achieve a primary particle size fraction of 6 – 45 µm which was tested under adsorption alone and UV irradiation experiments. The decreased STC primary particle size more closely simulated a particle suspension similar to that of the TiO$_2$. These results were compared to the STC-0.25-12, 45 – 90 µm size fraction results from Figure 5-4c in Figure 5-6.

Decreased particle size increased Hg removal under 30 minutes. Hg removal begins to reach pseudo equilibrium after only 5 minutes for a size fraction of 6 – 45 µm versus an hour for 45 – 90 µm for STC-0.25-12. Additionally, the Hg removal difference between adsorption alone and photocatalysis decreased with decreasing primary particle size. By decreasing the particle
size, more UV photons could be absorbed or refracted to decrease Hg reduction photochemistry and an increased interaction between adsorbent and adsorbate increased Hg adsorption in less time than for a larger STC particle. Therefore, Hg removal by STC is preferential to divalent Hg and smaller particle size.

Figure 5-6. Comparison of different primary particle sizes of STC-0.25-12 100 µg/L Hg removal via adsorption and photocatalysis.

While decreasing the STC particle size helped elucidate Hg removal phenomena, it may not be desired for a commercial treatment system since it would require greater energy to separate the adsorption particles from solution. Therefore, the STC was altered using pore size and TiO₂ loading to achieve greater Hg removal than with STC-0.25-12.

**Effect of TiO₂ surface area and pore size**

Both pore size and TiO₂ loading were increased from previously tested STC-0.25-12 to create STC-2-60 resuming the use of a larger primary particle size fraction of 45 – 90 µm. The results of STC-2-60 applied to Hg removal are shown in Figure 5-7 and compared to STC-0.25-12 results from Figure 5-4c. By increasing pore size and TiO₂ loading, Hg removal was increased. Other conformations of STC with TiO₂ mass loadings of 12 and 60% shown in Table
4-2 were also tested and did not achieve Hg removals greater than STC-2-60. Again, in the presence of UV, Hg removal is slightly worse than adsorption alone with STC-2-60. The added energy of the UV light did not provide a benefit towards Hg removal with STC.

Figure 5-7. Comparison of STC-0.25-12 to STC-2-60 for 100 µg/L Hg removal via adsorption and photocatalysis.

To further understand the STC properties responsible for an increase in Hg removal at 60 minutes via adsorption alone, Hg removal was plotted versus various material properties (STC surface area, available TiO₂ surface area, and average pore diameter) in Figures 5-8 through 5-10. Comparing the specific surface areas of the two materials, STC-2-60 has the lowest specific surface area of all the material but performs the best (Figure 5-8). However, the total specific surface area of the composite is not directly related to the specific surface area of available TiO₂. STC-2-60 has more available TiO₂ surface area and therefore adsorption sites than that of all the other STC (Figure 5-9). Therefore, Hg removal is influenced by the fraction of TiO₂ specific surface area and not the silica specific surface area. It can be concluded that the majority of Hg is adsorbing to the TiO₂. Additionally, STC-2-60 does have a larger average pore diameter than STC-0.25-12 which can increase pore diffusion and therefore a more rapid removal of Hg.
Interestingly, when Hg removal is graphed versus average pore diameter, there is an influence (Figure 5-10). There seems to be a preferable range of pore diameters around 50 to 175 Å. Once the pore diameter increased to over 250 Å, Hg removal was quickly diminished.
Figure 5-10. 100 µg/L Hg removal at 60 minutes by various STC formulations based on their analyzed STC average pore diameter (percentages indicate %wt TiO\textsubscript{2} in the composite)

### Optimization of STC

Once Hg removal was correlated with the available surface area of DP25 TiO\textsubscript{2} immobilized in silica macrosupports, further studies were desired to see to what extent Hg removal could be achieved. Thus far, the lowest concentration reached, by applying STC-2-60 under adsorption conditions, was 2.1 µg/L Hg. While this is 98% removal, it does not reach the target concentration. Therefore, using the existing STC formulation, two attempts were made to increase Hg removal. First, a higher loading of 70 %wt TiO\textsubscript{2} STC (STC-2-70) as used above in the Chapter 4 was tested for Hg removal under adsorption only conditions. Additionally, STC-4-60, a larger average pore size material was tested (Figure 5-11).

As in comparison to the best performing STC from previous studies (STC-2-60), Hg removal for STC-2-70 is very similar. It does not appear that the increase in available TiO\textsubscript{2}...
Figure 5-11. Comparison of STC-2-70 and STC-4-60 to STC-2-60 for 100 µg/L Hg removal via adsorption.

surface area improved Hg capacity beyond that already reached by STC-2-60. STC-4-60, however with an average pore diameter almost twice that of STC-2-60 (Table 4-2 and 4-4) had significantly reduced Hg removal verifying the conclusion from Figure 5-10 that an optimal pore diameter range exists. Also referring back to the measured available TiO$_2$ surface area in Figure 4-13, only small improvements were made in the TiO$_2$ surface area resulting in a lack of improved Hg removal.

Another attempt was made to optimize the STC by altering the dopant characteristics. As noted above, three different synthesis procedures were completed to produce TiO$_2$. Methylene blue (MB), a well studied textile dye, was used as a probe for the adsorption and photocatalytic capabilities of each of these produced titania materials (Figure 5-12). Methylene blue is a divalent cationic dye, and could be a good indicator for Hg adsorption extent.
While SA(450), TPT(450), and QHZ(450) all exhibited photocatalytic activity indicating crystalline development after calcination, this activity or the adsorption properties were not greater than that of DP25. In addition, the surface area (Table 4-3) and the functionality (Figure 4-10) of the materials was not greatly improved from that of DP25 TiO$_2$ either. Therefore, these materials were not immobilized in silica. While CQHZ did not appear to be photoactive, its high surface area and large affinity for MB showed promise for use as a Hg sorbent. This material was used to produce STC-2-60CQHZ. The material was then tested for Hg removal under batch adsorption only conditions (Figure 5-13).

Again, the attempt at material optimization did not result in increased Hg removal under the time studied. While QHZ media had a higher surface area, when it was doped in the silica matrix, the resulting available surface groups were very similar to that of STC-2-60 (Figure 4-10). The optimal material for Hg removal in batch studies with Hg(NO$_3$)$_2$ was determined to be STC-2-60 resulting in a Hg final concentration of 2 µg/L in 60 minutes.
Mercury Removal: Hg(NO₃)₂ vs. HgCl₂ vs. Hg(OAc)₂

Solutions of Hg nitrate represent the simplest solution chemistry for Hg removal studies. However, as noted in the literature review, this un-complexed simple speciation will most likely not exist in wastewater effluents or the natural environment. Therefore, it was desirable to determine the extent of Hg removal by STC adsorption with a more complex solution chemistry.

The impact of media loading on pseudo equilibrium removal of Hg by adsorption from 100 µg/L aqueous solutions onto STC-2-60 (the highest performing STC) was compared based on the Hg precursor used to create the Hg solutions (Figure 5-14). The scale of C/C₀ was magnified to show differences. After 24 hours, greater than 99% of total aqueous Hg was removed for all species reaching a low concentration of 1.0 µg/L Hg.

While the speciation of Hg in solution did not greatly change the extent of Hg removal at pseudo equilibrium, a time study was performed with 100 µg/L of Hg prepared with HgCl₂ to determine if Hg removal versus time was impacted. First, the STC tested initially (STC-0.25-12)
with Hg(NO$_3$)$_2$ solutions and the parent compounds (silica-0.25 and DP25) were tested (Figure 5-15).

Figure 5-14. Comparison of initial mercury speciation on 100 µg/L Hg removal by STC-2-50 via adsorption

Figure 5-15. Comparison of 100 µg/L Hg from solutions of HgCl$_2$ via adsorption
Comparing Hg removal trends for Hg(NO$_3$)$_2$ solutions (Figure 5-2a) with those of HgCl$_2$ solutions, silica-0.25 performed the same Hg removal, however, Hg removal for both DP25 and STC-0.25-12 from HgCl$_2$ solutions versus Hg(NO$_3$)$_2$ solutions was about 20% less. However, once the STC was modified to STC-2-60 (Figure 5-16), Hg removal again increased to the level that was noted in the Hg(NO$_3$)$_2$ studies. The larger open pore network of the STC-2 material with a greater available TiO$_2$ surface area facilitates rapid uptake of Hg species.

![Figure 5-16. Comparison of 100 µg/L Hg from solutions of HgCl$_2$ via adsorption](image)

**Mercury Removal of a Sampled Effluent**

As Hg concentrations in the environment continue to increase, advanced water treatment of drinking water may be required to protect human health. Additionally, as water becomes an even scarcer commodity, it may be necessary to directly reuse water reclamation facilities discharge for potable applications. An effluent water sample was collected from the University of Florida’s Water Reclamation Facility to investigate the impact of this water matrix on Hg removal via adsorption onto STC. Actual Hg concentrations in the effluent were not detectable.
with method 254.3 on the AA, so the water was spiked with a Hg(NO$_3$)$_2$ solution to achieve a total Hg concentration of 100 µg/L. It was hypothesized that in these studies, different trends with respect to adsorption alone versus photocatalysis may be realized due to the presence of organic compounds, variation in pH, and chlorides. An initial measurement found 5.0 mg/L of non-purgable total organic carbon (TOC), an average pH of 7, and a chloride concentration of 45 mg/L.

**Batch testing**

Both STC-0.25-12 and STC-2-60 were tested under adsorption alone (in the dark) and photocatalysis conditions in the presence of 254 nm irradiation in the batch configuration. Hg removal from the UF Water Reclamation Facility reached 75% with the STC-2-60 after 30 minutes (Figure 5-17).

![Figure 5-17. Hg removal from UF Water Reclamation Facility effluent spiked with 100 µg/L Hg via adsorption, 45 – 90 µm size fractions STC](image)

The result of adding competitive ions to the water chemistry was a decrease in Hg removal by 20% from that of the Hg(NO$_3$)$_2$-deionized water solutions. This result agrees with that of
Figure 5-15 using HgCl₂ as the initial Hg. Therefore, Hg formed complexes with chloride that were subsequently removed. The presence of UV illumination, on the other hand, did not achieve any Hg removal for either STC formulation even after 60 minutes of exposure (Figure 5-18).

![Graph](image1.png)

Figure 5-18. Hg removal from UF Water Reclamation Facility effluent spiked with 100 µg/L Hg via photocatalysis, 45 – 90 μm size fractions STC

![Graph](image2.png)

Figure 5-19. TOC trends during Hg removal by photocatalysis (UV) of UF Water Reclamation Facility effluent spiked with 100 µg/L Hg
Organic matter was monitored during the reaction period with UV and STC-2-60 by measuring TOC concentrations (Figure-5-19). STC-2-60 did prove to be a successful photocatalytic oxidant of organic matter with first order kinetic destruction of TOC in exchange for a loss of Hg capacity. Due to the photocatalytic activity, TiO$_2$ adsorption sites were likely no longer available for Hg adsorption.

**Continuous flow**

Based on results from the batch studies, two column tests were performed to test the feasibility of using a fixed bed reactor to remove Hg. The optimal parameters selected were: adsorption alone, STC-2-60, and a 20 minute empty bed contact time. After a desired volume of Hg solution had been tested, a 5% HCl acid rinse was introduced to the column to regenerate the pellets. Following, additional Hg removal runs were performed. On the first run, STC-2-60 achieved about 65% Hg removal (Figure 5-20).

![Figure 5-20. Continuous flow Hg removal from synthetic solutions via adsorption alone, pellet size fraction, STC-2-60, 20 minute residence time 100 µg/L Hg](image)

Due to the larger primary particle size of the STC, a reduction in Hg removal was seen from the batch studies. The second run, after regeneration which removed approximately 87% of...
the sorbed Hg, resulted in about 45% Hg removal. Hg removal was maintained and slightly improved for over 4 hours when the test was terminated. A second column study was performed with a faster residence time of 2.5 minutes to test larger flow volumes (Figure 5-21). This study did not achieve significant Hg removal.

Figure 5-21. Continuous flow Hg removal from synthetic solutions via adsorption alone, pellet size fraction, STC-2-60 minute residence time 100 µg/L Hg
CHAPTER 6
PHOTOCHEMICAL REACTIONS OF TRACE LEVEL AQUEOUS MERCURY

Introduction

Photochemical reactions have long been recognized as important processes in water chemistry,\textsuperscript{140} in that the absorption of light by dissolved compounds leads to the generation of chemical reactions that change solution chemistry. These principles have been applied for water and wastewater treatment for many organic and inorganic pollutants.\textsuperscript{141-143} While the photochemistry of Hg with regards to dissolved gaseous mercury (DGM) production has been studied primarily in natural aquatic systems as reviewed, it is plausible to utilize these reactions for the treatment of Hg contaminated waters to achieve sub-µg/L concentrations. Laboratory studies with prepared aqueous Hg solutions have not been well explored and were generally related to Hg cycling in the environment. These studies included UV-exposure of Hg(OH)\textsubscript{2} solutions prepared in deionized water followed by DGM removal by purging with inert gases.\textsuperscript{144,145,146} Herein, laboratory studies of Hg removal from aqueous solutions through photochemistry are discussed and emphasize: (1) Hg reduction and volatilization to produce aqueous concentrations < 2 µg/L, and (2) improved understanding of Hg aqueous photochemistry for potential application in water treatment technologies.

Control Experiments

Hg studies were completed in 100 mL batch reactors (Figure 3-1) with 254 or 365 nm UV bulbs and the available gas ports using solutions of Hg(NO\textsubscript{3})\textsubscript{2}. To ensure that Hg loss from solution was attributed to photochemical processes, a series of control experiments were performed using the lowest initial concentration (50 µg/L) and the longest reaction time (60 minutes) studied as these conditions had the highest UV to Hg ratio. First, the Hg solution without UV illumination (in the dark) was purged with nitrogen, the most reducing conditions

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studied here, to ensure that there was no Hg loss due to purging alone. Another control at each UV wavelength but with no purge was also performed to ensure there was no Hg loss due to UV alone. The results in Table 6-1 show that, the controls, with either a purge or UV, did not remove appreciable quantities of Hg and were comparable to a blank where there was no purge or UV. Once both the purge and UV irradiation were introduced simultaneously, Hg concentrations diminished in the aqueous phase almost completely in 60 minutes. The decrease in Hg concentration is attributed to the reduction of ionic Hg to Hg\(^0\) and subsequent volatilization of Hg\(^0\) from solution in the purge gas.\(^{147}\) As further verification that volatilization of Hg occurred, the difference between filtered and unfiltered samples was not significant, therefore no filterable species of Hg greater than 0.45 µm were formed via photochemical reactions. In addition, after the reaction period, the reactor was filled with 100 mL of 10% nitric acid and allowed to equilibrate for 24 hours. The acid was subsequently analyzed for Hg. The Hg concentration was less than 1% of the starting concentration, verifying that adsorption of Hg to the vessel walls was not a significant factor in Hg removal. In conclusion, photochemical reactions are responsible for the transformation of ionic Hg to elemental Hg which is transferred to the purge gas and removed from the aqueous solution. Normalized concentrations therefore represent the fraction of total Hg remaining in solution which is the sum of ionic Hg and non-volatilized elemental Hg. One minus the normalized concentration represents the fraction of Hg that was reduced to elemental Hg and volatilized from solution in the purge gas.

<table>
<thead>
<tr>
<th>Condition</th>
<th>C/C(_0)</th>
<th>Range</th>
<th>Sample Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>No UV, no purge</td>
<td>0.96</td>
<td>0.01</td>
<td>Unfiltered</td>
</tr>
<tr>
<td>Nitrogen purge, no UV</td>
<td>0.97</td>
<td>0.06</td>
<td>Unfiltered</td>
</tr>
<tr>
<td>No purge, 365 nm UV</td>
<td>0.88</td>
<td>0.05</td>
<td>Unfiltered</td>
</tr>
<tr>
<td>No purge, 254 nm UV</td>
<td>0.97</td>
<td>0.02</td>
<td>Unfiltered</td>
</tr>
</tbody>
</table>
Table 6-1. Continued

<table>
<thead>
<tr>
<th>Nitrogen Purge, 365 nm UV</th>
<th>0.02</th>
<th>0.01</th>
<th>Unfiltered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen Purge, 254 nm UV</td>
<td>0.01</td>
<td>0.00</td>
<td>Filtered</td>
</tr>
</tbody>
</table>

**Reaction Mechanisms**

Many redox reaction mechanisms have been suggested in the literature and have been recently reviewed. Based on the references cited here and other relevant photochemistry literature and testing in a simple system of H$_2$O and Hg(NO$_3$)$_2$ (the lack of DOC, iron, chloride and semiconductors) the plausible reaction mechanisms were determined to be those shown in Table 6-2.

Table 6-2. Hg photochemistry reaction mechanisms

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxidation</strong></td>
<td></td>
</tr>
<tr>
<td>$Hg^0 \rightarrow Hg^{2+} + products$</td>
<td>(Zhang 2001)</td>
</tr>
<tr>
<td>$Hg^0 + 2 \cdot OH \rightarrow Hg^{2+} + 2OH^-$</td>
<td>(Zepp 1987)</td>
</tr>
<tr>
<td>$Hg^0 + \cdot OH \rightarrow HgOH$</td>
<td>(Munthe 2001)</td>
</tr>
<tr>
<td>$\cdot HgOH + \cdot OH \rightarrow Hg(OH)_2$</td>
<td>(Gardfeldt 2001)</td>
</tr>
<tr>
<td>$\cdot HgOH + O_2 + H_2O \rightarrow Hg(OH)_2 + H^+ + O_2^-$</td>
<td>(Gardfeldt 2001)</td>
</tr>
<tr>
<td>$2 \cdot HgOH \rightarrow Hg(OH)_2$</td>
<td>(Gardfeldt 2001)</td>
</tr>
<tr>
<td><strong>Reduction</strong></td>
<td></td>
</tr>
<tr>
<td>$Hg(OH)_2 \rightarrow Hg^0 + products$</td>
<td>(Munthe 2001)</td>
</tr>
<tr>
<td>$Hg^0 + \cdot OH \rightarrow HgOH$</td>
<td>(Gardfeldt 2001)</td>
</tr>
<tr>
<td>$\cdot HgOH \rightarrow Hg^0 + products$</td>
<td>(Munthe 2001)</td>
</tr>
<tr>
<td><strong>Ancillary</strong></td>
<td></td>
</tr>
<tr>
<td>$NO_3^- \rightarrow NO_2 + \cdot O^-$</td>
<td>(Zepp 1987)</td>
</tr>
<tr>
<td>$\cdot O^- + H_2O \rightarrow \cdot OH + OH^-$</td>
<td>(Zepp 1987)</td>
</tr>
</tbody>
</table>

Therefore, direct photolysis of Hg was considered to play a primary role in reaction mechanisms. All reactions were assumed to occur simultaneously, therefore, Hg removed from solution was the net production of Hg$^0$. It was hypothesized that with an increase in oxygen exposure to the Hg solutions, Hg removal from solution would decrease due to an increase in
oxidation reactions or a loss of $O_2$ in the system. Additionally, it was predicted that as initial Hg concentrations increased, under the same light intensity, less reduction reactions would occur and less elemental Hg would be evolved from solution. As Hg concentrations increase, so does that of $NO_3^-$. Greater concentrations of $NO_3^-$ should contribute to more hydroxyl radical production and therefore more oxidation reactions with Hg. The production of hydroxyl radicals from $NO_3^-$ will also be impacted by the wavelength of light. At lower wavelengths, the compound has a higher molar absorptivity coefficient so more reactions to produce hydroxyl radicals will occur. This may account for the reason why the 365 nm UV control without a purge (Table 6-1) exhibited a slightly lower concentration of Hg. With less oxidants in solution, Hg could remain in the reduced state ($Hg^0$) longer and partition to the air in the void space above the reactor solution contributing to a small loss of Hg.

**In-Situ Purging and UV Irradiation**

**Effect of Initial Concentration**

Hg solutions of 50, 100, 500 and 1,000 µg/L were exposed to a 365 nm UV bulb and a nitrogen purge simultaneously. The results (Figure 6-1a) show that as Hg concentration increased, there was a decrease in Hg removal. However, even with 1,000 µg/L Hg, over 60% of the aqueous divalent Hg was reduced to elemental Hg and removed from solution in one hour. The lowest Hg concentration reached was 1 µg/L for the initial concentration of 50 µg/L after 60 minutes.

There does seem to be a marked change in reaction kinetics with the initial concentration of 50 µg/L compared to the higher concentrations. At a closer investigation, for initial concentrations of 100 µg/L and less, the reaction is best modeled by first order reaction kinetics. Both higher concentrations however are better described by near zero order. There is likely a limited number of reduction reactions which can occur under 365 nm irradiation causing the
reaction rate to be independent of divalent Hg concentrations until a low enough molarity is reached.

Figure 6-1. Normalized aqueous Hg concentration verses time in the presence of a N₂ purge (2 L/min/100 mL) with four initial Hg concentrations: 50, 100, 500, and 1000 µg/L Hg and a) 365 nm UV or b) 254 nm UV

The UV wavelength was decreased to 254 nm with the expectation that it would provide more photon energy and intensity (2.46×10⁵ einsteins/min for the 254 nm lamp compared to 1.25×10⁵ einsteins/min for the 365 nm lamp) for photoreactions and therefore more Hg could be reduced and therefore purged from solution (Figure 6-1b). A similar trend existed as with the 365 nm bulb (Figure 6-1a) but a greater percentage of Hg was removed at higher concentrations and demonstrates first order kinetics. While the 50 µg/L removal profiles look very similar, the
rate constants are 0.18 s\(^{-1}\) for 254 nm versus 0.11 s\(^{-1}\) for 365 nm, showing a faster conversion to elemental Hg under the shorter wavelength irradiation (Table 6.3). A slightly lower Hg concentration of 0.4 µg/L was reached after 60 minutes of 254 nm UV exposure and an initial concentration of 50 µg/L. Despite the possibility of an increased production of hydroxyl radicals through NO3\(^-\) reactions with a shorter wavelength of light, more Hg is reduced with 254 nm than 354 nm. Using a short wavelength UV irradiation with an inert purge gas, significant quantities of divalent aqueous Hg can be volatilized to the gas phase with a large range of Hg concentrations.

Table 6-3. Reaction rate constants for varying initial Hg concentration under a nitrogen purge

<table>
<thead>
<tr>
<th>Initial Hg (µg/L)</th>
<th>Rate Order</th>
<th>Rate Constant</th>
<th>Fit (R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>365 nm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>First</td>
<td>0.11 s(^{-1})</td>
<td>0.996</td>
</tr>
<tr>
<td>100</td>
<td>First</td>
<td>0.029 s(^{-1})</td>
<td>0.989</td>
</tr>
<tr>
<td>500</td>
<td>Zero</td>
<td>4*10^-8 M-s(^{-1})</td>
<td>0.994</td>
</tr>
<tr>
<td>1000</td>
<td>Zero</td>
<td>5*10^-8 M-s(^{-1})</td>
<td>0.948</td>
</tr>
<tr>
<td>254 nm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>First</td>
<td>0.182 s(^{-1})</td>
<td>0.994</td>
</tr>
<tr>
<td>100</td>
<td>First</td>
<td>0.118 s(^{-1})</td>
<td>0.962</td>
</tr>
<tr>
<td>500</td>
<td>First</td>
<td>0.031 s(^{-1})</td>
<td>0.986</td>
</tr>
<tr>
<td>1000</td>
<td>First</td>
<td>0.053 s(^{-1})</td>
<td>0.994</td>
</tr>
</tbody>
</table>

**Effect of Purge Gas**

The literature supports that the presence of oxygen promotes oxidation of Hg and generally results in decreased DGM concentrations\(^5\). To determine the extent of oxidation versus reduction with increased oxygen concentration, the purge gas was changed from nitrogen to air in one experiment to oxygen in another.

Theoretical dissolved oxygen concentrations (DO), calculated using Henry’s Law, are about zero for nitrogen, 8 mg/L for air, and saturated (40 mg/L) for the oxygen purge. These DO levels should be reached under or close to 5 minutes reaction time due to the high delivery flow.
rate of the gas into the 100 mL reactor volume. Figure 6-2a illustrates the impact of purge gas on 365 nm irradiated 50 μg/L Hg solutions.

Figure 6-2. Normalized aqueous Hg concentration verses time of 50 μg/L Hg in the presence of three different purge gases (2 L/min/100 mL): nitrogen (N2), air (Air), and oxygen (O2) and a) 365 nm UV or b) 254 nm UV

As anticipated, as DO levels increased, Hg removal decreased resulting from either an increase in Hg oxidation reactions and/or a decrease in Hg reduction reactions (where electrons were scavenged by oxygen). Interestingly, independent of the DO, both air and oxygen purged solutions lost 80% of the total Hg to the air phase after 60 minutes with very similar rates. The rates of Hg reduction in the presence of oxygen were markedly slower at approximately 0.03 s⁻¹
versus 0.11 s\(^{-1}\) for an oxygen depleted environment using first order kinetic modeling (Table 6-4).

<table>
<thead>
<tr>
<th>Purge gas</th>
<th>Rate Order</th>
<th>Rate Constant</th>
<th>Fit ((R^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>365 nm</td>
<td>Nitrogen</td>
<td>First</td>
<td>0.111 s(^{-1})</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>First</td>
<td>0.033 s(^{-1})</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>First</td>
<td>0.030 s(^{-1})</td>
</tr>
<tr>
<td>254 nm</td>
<td>Nitrogen</td>
<td>First</td>
<td>0.183 s(^{-1})</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>First</td>
<td>0.006 s(^{-1})</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>First</td>
<td>0.020 s(^{-1})</td>
</tr>
</tbody>
</table>

Each purge gas was also tested with 254 nm UV irradiation of 50 µg/L Hg solutions (Figure 6-2b). Here, an interesting phenomenon was observed. The air-purged solution had less Hg removal than that of an oxygen purge. There is potential for dissolved species from the carbon dioxide purge present at pH 4 to have an impact on photochemical reactions. As compared to the 365 nm irradiated solutions, the impact of dissolved oxygen is also more pronounced with shorter wavelength irradiation as indicated by a further decrease in reaction rate. Here, first order reaction rates are only 0.006 s\(^{-1}\) and 0.020 s\(^{-1}\) for air and oxygen purges respectively (Table 6-4).

**Effect of Purge Rate**

While the balance of reduction/oxidation reactions can be managed to some extent, the purge parameters can be altered to control Hg evasion from solution. Amyot et al. concluded that in natural systems, wind speed is more important than DGM levels to the flux of Hg leaving the water body.\(^{51}\) While the ratio of volatilized compounds to purge rate will be directly related for high vapor pressure compounds, it is especially important in the studied Hg photochemistry systems since reduction and oxidation reactions occur simultaneously. The faster and more
efficiently elemental Hg can be transferred to the gas phase and volatilized, the less oxidation reactions can occur.

To test the impact of purge rate on Hg volatilization, experiments were performed with 100 µg/L Hg solutions so that an improvement in reaction rate could be easily measured. From preliminary studies, it was confirmed that as the purge rate in the reactor increased, so did the Hg removal rate. The purge rate of 2 L/min, used in all the above experiments, was the largest purge flow that could be achieved within the confines of the batch reactor (Figure 3-1). From here, to increase the liquid-gas interface, a porous glass frit was installed on the end of the ¼ inch glass purge tube to decrease the purge bubble size. Figure 6-3a shows that under 365 nm irradiation the Hg removal increased significantly with time once the liquid-gas interface was increased for both a nitrogen and an air purge. Near complete removal was reached in 60 minutes with the glass frit (below the MDL) versus 20% Hg remaining in solution with the glass tube. With this removal rate increase, the glass frit was applied to 254 nm irradiated solutions (Figure 6-3b). Here an improvement in Hg reduction rate was also noted to achieve a Hg concentration below the MDL. Even the air purged system, which previously had very poor removal with a glass tube purge, Hg removal was increased over 15% by applying a smaller bubble size purge. Reaction rate constants were determined using first-order models and further demonstrate the increase in Hg\(^0\) production and evasion (Table 6-5). It is possible that Hg levels could have been reduced to levels low enough to meet the Great Lakes standards as levels below the capabilities of the AA technology were reached.

To further this concept, the reaction mechanism needs to be identified. Therefore, a larger number of variables should be studied. This would include nitrate and nitrite as well as free atoms or radicals of hydrogen and oxygen which could be playing a role.
Figure 6-3. Normalized aqueous Hg concentration versus time of 100 µg/L Hg solutions for two different purge gases (2 L/min/100 mL), nitrogen (N\textsubscript{2}), air (Air) and two different bubble sizes, large (tube) and small (frit) in the presence of a) 365 nm UV or b) 254 nm.
Table 6-5. Reaction rate constants for 100 µg/L Hg irradiated solutions comparing purge gas (2 L/min/100 mL) delivery device

<table>
<thead>
<tr>
<th>Purge</th>
<th>Purge delivery</th>
<th>Rate Order</th>
<th>Rate Constant</th>
<th>Fit (R²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>365 nm</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen purge*</td>
<td>Tube</td>
<td>First</td>
<td>0.029 s⁻¹</td>
<td>0.989</td>
</tr>
<tr>
<td>Nitrogen purge</td>
<td>Frit</td>
<td>First</td>
<td>0.065 s⁻¹</td>
<td>0.989</td>
</tr>
<tr>
<td>Air purge</td>
<td>Tube</td>
<td>First</td>
<td>0.016 s⁻¹</td>
<td>0.972</td>
</tr>
<tr>
<td>Air purge</td>
<td>Frit</td>
<td>First</td>
<td>0.070 s⁻¹</td>
<td>0.958</td>
</tr>
<tr>
<td><strong>254 nm</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen purge*</td>
<td>Tube</td>
<td>First</td>
<td>0.118 s⁻¹</td>
<td>0.994</td>
</tr>
<tr>
<td>Nitrogen purge</td>
<td>Frit</td>
<td>First</td>
<td>0.161 s⁻¹</td>
<td>0.992</td>
</tr>
<tr>
<td>Air purge</td>
<td>Tube</td>
<td>First</td>
<td>0.003 s⁻¹</td>
<td>0.844</td>
</tr>
<tr>
<td>Air purge</td>
<td>Frit</td>
<td>First</td>
<td>0.008 s⁻¹</td>
<td>0.984</td>
</tr>
</tbody>
</table>

*also presented in Table 6-3*
CHAPTER 7
CONCLUSIONS

The STC created using a synthesis method involving HF catalysis and pre-manufactured DP25 possessed a broad range of physical characteristics. By increasing HF concentration, average pore diameters were enlarged from 46 to 253 Å resulting in specific surface area decrease and pore volume increase. Further, TiO₂ addition decreased specific surface area and pore volume. A large proportion of the TiO₂ was found to be available on the surface of the STC (up to 87%) and more surface area was available with increased TiO₂ loading. While these changes are broad, the IEP, TiO₂ particle size and band gap energies of the STC were not largely affected.

Hg removal down to 2.1 µg/L can be achieved with STC-2-50 with decreased energy requirements for filtration as compared to TiO₂ alone. The combination of silica and TiO₂ provides a macrosorbent with cation electrostatic attraction to achieve a high degree of trace level aqueous Hg removal by adsorption. Contrary to previous assumptions, photocatalysis of trace level Hg was not more successful than adsorption alone. The production of elemental Hg produced by photochemical reactions caused delayed Hg removal compared to adsorption alone for STC-0.25-12. With no STC formulation did the presence of UV lead to enhance removal over that of adsorption alone. Effluent water with TOC and chloride contributions from the University of Florida Water Reclamation Facility, were tested with STC-2-60 and resulted in 60% Hg removal to reach a concentration of about 40 µg/L was achieved by adsorption. This technology is promising and could be applied for the treatment of Hg burdened waters such as contaminated groundwaters from industrial activity, effluent from Chlor-alkali facilities employing a Hg cell process, flue gas desulfurization liquids and others. However, further Hg removal would be required to meet Great Lakes standards.
Hg removal through photochemical reduction followed by volatilization in a purge gas was found to be most successful with lower concentrations of Hg with a higher energetic wavelength of 254 nm and a nitrogen purge gas. While understanding the reaction mechanisms of DGM production is important for the bioavailability of Hg in natural systems, the use of photochemical reactions in the application of a treatment technology is also of interest. The selective removal of trace level aqueous Hg using traditional treatment technologies such as precipitation, ion exchange, or adsorption processes can become very difficult and cost intensive. A possible technology pathway could be the reduction and volatilization of Hg from aqueous solution using a gas purge and UV light followed by air phase capture such as that applied for gaseous Hg removal at ambient conditions from Chlor-alkali manufacturing facilities or low temperature condensation. There is promise with this technique to reach 1.3 ng/L Hg concentrations since Hg was removed to below detection limits using AA instrumentation.

In summary, the most effective treatment method will depend on the water chemistry, Hg concentration, and allowable design parameters. While in-situ purging produced the lowest Hg concentrations after treatment, this still requires post-treatment. Additionally, STC could achieve significant Hg removal in very short times (such as 5 minutes).

Contributions to Science

- Demonstrated the robust nature of STC which could be altered for TiO₂ loading and pore size with significant changes in physical structure (specific surface area, pore diameter, pore volume and available TiO₂ surface area) but not chemical properties (crystalline nature, crystalline size, PZC)
- Found that photocatalytic reactions for the removal of aqueous Hg at trace level concentrations was not advantageous over adsorption based on photochemical reactions that reduce Hg to elemental which has poor sorption properties for STC
- Identified STC-2-60 as an optimal formulation for trace level aqueous Hg removal, above which Hg removal could not be further increased by TiO₂ addition or pore size increase.
• Demonstrated that STC could be used as a Hg removal technology for such applications as treatment of water reclamation facility effluents

• Increased understanding of Hg photochemistry by 1) verifying that even 1 mg/L solution of Hg produced from Hg(NO₃)₂ could result in significant Hg reduction and volatilization from solution and 2) realizing that even under extremely oxidizing conditions (solutions saturated with oxygen) trace levels of Hg could be reduced and removed from solution.

Future Recommendations

• Further understanding of trace level Hg adsorption mechanisms through sequential extraction and instrumentation analyses.

• Test more synthesis procedures for STC and their impacts on material properties (such as co-condensation and TMOS precursor).

• Perform an economic analysis on use of TiO₂ versus STC with respect to initial capital cost and energy consumption for solids separation.

• Further understanding of reaction mechanisms for Hg photochemistry reactions through the measurement of key compounds that are photoactive and through studying the impact of Hg speciation of Hg reduction kinetics.

• Apply Hg control technologies for air phase capture of Hg once it has been volatized with photochemical reactions.
APPENDIX A

ADSORPTION AND PHOTOCATALYSIS

Initial Hg testing commenced with 100 µg/L Hg concentrations prepared from Hg(NO₃)₂ employed in the same batch reactor as previously shown in Chapter 3 (Figure 3-1). The tests presented here were completed before the production of STC changed to include wash-sieving. Some interesting trends were noticed and are presented here. However, once kinetic studies were commenced, test results could not be reproduced accurately and the method was changed resulting in the data presented in Chapter 5. The poor reproducibility was believed to be a symptom of residual TOC content from the STC production (residual ethanol) in combination with an inconsistent particle size distribution.

Initial test conditions were based on previous photocatalytic Hg removal tests found in the literature. Dissolved oxygen (DO) was shown to significantly hinder the reduction rates of Hg by photocatalysis, therefore oxygen concentration was altered by a nitrogen or air purge resulting in approximate DO levels of 2 and 7 mg/L respectively in the initial solution before testing commenced. A replacement hole scavenger, citric acid, was used to block the electron-hole recombination and further increase Hg reduction rates. An optimal reaction time was selected to be 15 minutes. Results are presented in Figure A-1. All data is represented with error bars showing the range from two replications. UV removal trends for TiO₂ agree with the previous literature findings. The removal of dissolved oxygen and addition of citric acid decreased the concentration of Hg remaining in the solution. In addition, and to the contrary, saturation with air instead of oxygen removal, further increased Hg removal as proposed by Tennakone. Percent removal was found to be lower here than in the literature, however, the concentration of Hg applied was one thousand times less than previously investigated. UV conditions with STC are not found in the literature. STC performed very poorly with UV only. However, in the
presence of citric acid, nitrogen purge or both, Hg removal increased to 40%. A further increase was realized with and air purge. Silica-1 on the other hand, did not show an affinity for Hg.

![Figure A-1. Photocatalysis of 100 µg/L Hg using 1 g/L media and when applicable a nitrogen gas purge, air purge, and/or 10 mg/L citric acid](image)

Adsorption under the same conditions but without the presence of UV and for 60 minutes was performed and the results are shown in Figure A-2. Adsorption with citric acid and a nitrogen purge achieved the best performance for all media types. The air purge did not perform better than the nitrogen purge in any scenario. While TiO₂ reached the lowest C/C₀ with UV illumination, the best results overall were with STC-1-30 without UV (i.e., adsorption only). Controls were carried out without media and resulted in an average C/C₀ value of greater than 0.9.

The literature notes that TiO₂ only achieves 30% removal of Hg at influent concentrations of 100 ppm in comparison to up to 100% removal via photocatalysis.¹⁵¹,¹⁵³,¹⁵⁴ However, at ppb concentrations used here, average removal of Hg for adsorption only performed better than UV for every media type.
Figure A-2. Adsorption of 100 µg/L Hg using 1 g/L media and when applicable a nitrogen gas purge, air purge, and/or 10 mg/L citric acid for 60 minutes.

In an attempt to understand how citric acid increased Hg removal under adsorption conditions, non-purgeable dissolved organic carbon (TOC) was analyzed for two systems, one with citric acid and one without (Figure A-3).

Figure A-3. Analysis of TOC trends with different media in adsorption only conditions with 100 µg/L Hg initial concentration and 10 mg/L citric acid where included.

The experiment was simplified by removing the nitrogen purge due to data showing enhanced removal with citric acid addition alone. The addition of 10 mg/L of citric acid (C₆H₈O₇) is
equivalent to 4.14 mg/L of TOC as shown with the red line on Figure A-3. It can be clearly seen that even without citric acid added to solution, there is a significant concentration of TOC in solution. This TOC contribution was attributed to water soluble organic compounds desorbing from the surface of the media into solution. Silica by far has the greatest contribution of TOC to solution. Also a small contribution was noted from filtering as indicated by the slight increased in TOC from the control to the control with filtering (ControlF).

The difference of the citric and no citric data points for each condition listed are shown in Table A-1. The quantity of citric is maintained except during the TiO\textsubscript{2} adsorption test. This would suggest that either TiO\textsubscript{2} adsorbs the citric acid which can act like a chelator for Hg ions or that a Hg citric complex forms which has a higher affinity for adsorbing to the TiO\textsubscript{2} surface.

A chemistry simulation using MinEQL+ was completed using 100 µg/L Hg initial concentration (from Hg(NO\textsubscript{3})\textsubscript{2}) and 10 mg/L of citric acid (Figure A-4). A Hg-citrate complex was predicted to be formed at the solution pH of 4. Additionally, since TiO\textsubscript{2} is positively charged at the solution pH (less than the PZC at about pH 6) and citric acid has a dominantly negative charge at pH 4 since it is in-between its pK\textsubscript{a1} and pK\textsubscript{a2}, adsorption of citric onto the TiO\textsubscript{2} is electrostatically favorable. Therefore, either situation is plausible. Silica and STC on the other hand will possess a negative surface charge at pH 4 so will not electrostatically attract the citric acid compounds as indicated by the retention of TOC in solution (Table A-1). However,
since there was other contribution of TOC besides that of citric acid, it can not be clearly
deduced that citric acid remained in solution. Therefore, from this data, it is uncertain how the
citric acid influences the STC in enhanced Hg removal.

Figure A-4. Mercury speciation with 100 µg/L Hg from Hg(NO$_3$)$_2$ in the presence of 10 mg/L
citric acid from MinEQL$^+$
APPENDIX B
pH ADJUSTMENT

Previous experiments in the literature also investigated the effect of pH on the adsorption and photoreduction of Hg. It was expected that an increase in pH would increase Hg removal in both adsorption and UV systems by creating or increasing favorable electrostatic attraction. The pH of a stock solution of Hg was adjusted with HNO₃ or NaOH. At first attempt, the removal of Hg did not seem to change with pH for silica and STC and increased slightly for TiO₂. However, at the termination of the test, the pH was dramatically different compared to the initial pH as a result of the media. By plotting the relative concentration versus the final pH (Figure A-5), a trend similar to the literature can be noted.

![Figure A-5. Final pH versus C/C₀ for pH adjusted 100 µg/L Hg solutions with 1 g/L media loadings for 60 minutes adsorption](image)

To account for the effect of the media, a second set of pH adjustments were performed with a new method. The pH of a 1 g/L media slurry in deionized water was adjusted to the desired pH and then spiked with Hg to achieve 100 µg/L of Hg. Here, the difference in the final pH from the targeted pH was smaller than when the pH of the Hg solution was altered and then
media was added. A dramatic decrease in remaining Hg occurred around pH 6 as seen in Figure A-6.

![Figure A-6. Final pH versus C/C₀ for pH adjusted 1 g/L media slurries spiked with 100 µg/L Hg for 60 minutes adsorption](image)

Additionally, the same conditions were tested with UV exposure as shown in Figure A-7. Again, the similar trend of increasing percent removal with increasing pH was seen with illumination of UV except for silica-1 which did not improve. The method of adjusting the pH of the media slurry has a uncertainty factor associated with it since there is no initial Hg sample and the true media loading is unknown (i.e., the exact spiked value is dependent on human and instrument accuracy and it can only be assumed the media was homogenously dispersed when it was distributed to the reactors). It should be noted that a pH difference between the silica-1, the STC-1-30 and TiO₂ exists after the addition of the same quantity of Hg. This could be an indication of the adsorption mechanism. As Hg hydrates, it increases the number of hydrogen ions in solution and decreases pH. However, if Hg is adsorbed as Hg^{2+} and loose OH⁻ groups, the pH would increase. It is also interesting to note the increase in C/C₀ with the addition of ions from the HNO₃ and NaOH used for pH adjustment (comparison of removal without pH adjustment versus pH adjusted removal at the same pH, ~ 4).
Figure A-7. Final pH versus C/C₀ for pH adjusted 1 g/L media slurries spiked with 100 µg/L Hg for 15 minutes UV irradiation
APPENDIX C
HEAT TREATMENT

To study the impact of surface functionaliation, the number of silanol groups was manipulated with heat treatment. This method was successfully illustrated by Zhuravlev who showed a decreasing coverage of hydroxyl groups on amorphous silica with increased vacuum treatment temperature up to 1100 °C\textsuperscript{155}. Three heat treatment temperatures were selected, 400, 550 and 1000 °C, and compared to a control (a STC of the same average pore size and TiO\textsubscript{2} loading with no additional heat treatment beyond that of production). Figure A-8 shows the evolution of the STC under the specified temperatures.

![Figure A-8. Evolution of Silica-1 and STC-1-30 under heat treatment and the resulting surface areas](image)

Physisorbed water is removed at approximately 180 °C. Recall that the drying process of the gels reaches this temperature. Therefore, the control STC would represent this category. Above 180 °C and until 400 °C dehydration occurs (i.e., removal of hydroxyl groups) but is also completely reversible. This range is represented by the 350 °C heat treated Silica-1 and STC-1-30. Above 400 °C, organic residuals have been destroyed. In the range of 500 to 800 °C, chemisorbed hydroxyl groups are further removed to an extent to reduce the material contact
angle and make the gel stable and ultraporous. This range is represented by the 550 °C heat treatment. Above 800 °C sintering begins as density increases and the pore volume fraction decreases. The highest heat treatment temperature of 1000 °C represents these changes. Another significant transformation occurs at 700 °C when TiO₂ begins to undergo a change from anatase form to rutile phase. This would only affect the STC-1-30 sample due to the presence of TiO₂. Figure A-8 also depicts the BET surface areas of the Silica-1 and STC-1-30 after heat treatment. Surface area did indeed decrease when the media was heat treated in the sintering regime.

A bottle point isotherm was performed on the heat treated samples to determine a relative change in the number of silanol groups; the amount of physisorbed water has been directly correlated to the quantity of surface silanols in previous literature. Two comparisons were made, the mass of water adsorbed per mass of media and the mass of water adsorbed per area of media. Both Silica-1 and STC-1-30 reacted to the heat treatment in the same manner as seen in Figure A-9.

![Figure A-9. Bottle point isotherm data for heat treated Silica-1 and STC-1-30](image-url)
The resulting materials were also analyzed with the Quantichrome NOVA for specific surface area (Figure A-10). The vertical lines indicate the shift from one heat treatment regime to the next. Silica and titania are affected by the corresponding regime as noted above. The specific surface areas of STC or silica were not reduced until sintering temperatures indicating that the change in water adsorption was indeed due to a change in surface functional groups.

![Figure A-10](image)

**Figure A-10.** Bottle point isotherm data for heat treated Silica-1 and STC-1-30 as measured by the Quantichrome NOVA. Vertical lines indicate shifts in heat treatment regimes.

On a mass per mass basis, the amount of silanol groups decreased with an increase in heat treatment temperature. The opposite was true when the amount of water adsorbed was normalized to surface area with the most noticeable change in the 1000 ºC heat treated STC. Therefore, the total number of silanol groups introduced to a batch system is less for the 1000 ºC heat treated STC, but the groups are physically closer together.

The heat treated STC was employed in UV and adsorption batch tests. Figure A-11 illustrates the results of the UV test. Minimum concentration of Hg left in solution was achieved by the 350 ºC heat treated Silica-1 and STC-1-30. Consistent with data above, STC-1-30 has a higher affinity for Hg than Silica-1.
Different results were found under adsorption conditions. There was no significant change in removal amount for the Silica-1 for each of the heat treatments. For the STC-1-30, heat treatments at 550 and 1000 °C equally achieved the best removal as seen in Figure A-12.

A large number of variables could account for the success or failure of the heat treatments. Under adsorption conditions, the decreased surface area or number of silanol groups did not
hinder Hg adsorption. However, since the silanol groups are closer together, two groups could interact with one Hg ion. Another factor to consider is that the number of silanol groups, while changing, could be in excess to the number of Hg ions that will react. Other factors include pH change, elimination of organic compounds, surface area and TiO₂ phase change. The effect of titania phase change was studied with titania alone. DP25 was heat treated at 1000 °C to accomplish conversion from anatase to rutile phase, then tested in batch conditions. The results are shown in Figure A-13. With adsorption only, the heat treated TiO₂ did not result in a higher efficiency for Hg removal. Under UV illumination there was no significant differences before and after heat treatment of the TiO₂. Therefore, Hg removal under either condition with 1000 °C heat treated STC-1-30 was not contributed to the phase change of TiO₂.

To further investigate Hg removal trends, the affect of pH was investigated. Average final pHs were very similar for all materials (± 1 pH unit). It is also not likely that pH changes this small were significant enough to change the Hg removal to a noticeable quantity. In addition, the concentration of TOC in these systems was investigated. A trend could not be identified.
between TOC concentration and Hg removal for heat treated STC. The same results were also found with the comparison of surface area with Hg removal. The final conclusion is that another parameter may not be identified or that silanol groups are the sole reason for a change in STC removal capacity.
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BIOGRAPHICAL SKETCH

Heather Elizabeth Byrne is the daughter of Barry and Laura Byrne born in Chicago, Ill. The family moved to Baltimore, MD in 1984, then again to Gainesville, FL in 1997. Here, Heather graduated from Buchholz High School in the year 2000. Directly following, Heather entered the University of Florida in the Department of Environmental Engineering Sciences. Five years later, with work experience from ESE, a Mactec company and a years worth of full time employment at Cargill Fertilizer Inc., Heather graduated Magna Cum Laude in the spring of 2005. Her honors thesis focused on mercury removal technologies from the Chlor-Alkali industry. This work was the beginning of Heather’s dissertation research. Heather performed that research under the guidance of David Mazyck in the same department. Through her class requirements, Heather also earned a Master of Engineering degree from the Department of Environmental Engineering Sciences in August of 2007.