

Coupling of Advanced Oxidation and Adsorption Processes onto Silica-Titania Composites for Low Level Capture of Metals from Water Effluents

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Table of Contents

Introduction 2
Literature Review..... 2
Materials and Methods 3
Results and Discussion..... 4
Conclusions 9
Future Studies 10
Planned Proposals based on Water Institute Funding..... 10
References 11

Table of Figures

Figure 1: Batch mercury removal from synthetic solutions via adsorption alone, 45 – 90 μm size fractions STC 5
Figure 2: Batch mercury removal from synthetic solutions via adsorption alone, 6 – 45 μm size fractions STC 5
Figure 3: Batch mercury removal from synthetic solutions via photocatalysis, 45 – 90 μm size fractions STC..... 6
Figure 4: Batch mercury removal from synthetic solutions via photocatalysis, 6 – 45 μm size fractions STC..... 6
Figure 5: Continuous flow mercury removal from synthetic solutions via adsorption alone, pellet size fraction 320 Å 32% STC, 20 minute residence time 7
Figure 6: Continuous flow mercury removal from synthetic solutions via adsorption alone, pellet size fraction 320 Å 32% STC, 2.5 minute residence time 7
Figure 7: Mercury removal from UF Water Reclamation Facility via adsorption, 45 – 90 μm size fractions STC 8
Figure 8: Mercury removal from UF Water Reclamation Facility via photocatalysis, 45 – 90 μm size fractions STC..... 8
Figure 9: Mercury adsorbed dependent upon initial mercury solution concentration and calcium sulfate mass loading 9

Introduction

Metals are non-biodegradable pollutants with well-documented adverse impacts on both ecosystem functions and human health. Currently, the EPA's priority pollutants list includes 13 metals, with mercury (Hg) and arsenic (As) being the most difficult to reduce to sub-ppb levels in wastewater effluents. New and more efficient technologies for water treatment are needed to help meet the increasingly stringent regulation for the protection of water resources and aquatic life. In this work, Hg was used as a case study to generate preliminary data that will support the development of a full proposal targeting competitive federal and/or state programs.

The applied treatment technology, Silica-Titania Composites (STC) (Mazyck et al., 2004), was developed at the University of Florida and has been commercialized for air-phase Hg recovery. The STC consist of a porous, high surface area silica-gel substrate ($> 600 \text{ m}^2/\text{g}$), which is transparent to UV light and impregnated with photocatalyst particles (i.e., TiO_2) (Mazyck et al., 2004). The technology focuses on the combination of adsorption and simultaneous or subsequent photocatalytic conversion (oxidation or reduction) for Hg removal. Adsorption on the silica-gel allows Hg to be concentrated while exposure of the TiO_2 to UV radiation ensures the conversion of adsorbed Hg to species that are more readily adsorbed, thus increasing the adsorption capacity of the STC compared to traditional sorbents. The STC can be tailored for particular applications by manipulating characteristics such as pore size distribution, surface chemistry, and TiO_2 loading. The effectiveness of silica-titania composites (STCs) was investigated specifically for the removal of low level mercury from water effluents. The completed work was expected to answer the following questions: (1) Is the STC technology effective in removing Hg from water? (2) What is the preferred system configuration? (3) What is the optimal STC formulation (e.g., pore size distribution, surface chemistry, titania loading) for Hg removal?

Literature Review

Hg is a widespread and persistent pollutant that has contaminated fisheries in the U.S. and worldwide. 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 (McDowell et al., 2004). This exposure can lead to adverse neurological effects, particularly in the developing fetus and during early childhood. There have been several health advisories on fish consumption in Florida since 1989 when a joint monitoring project was initiated by the Florida Fish and Wildlife Commission, Department of Environmental Protection, and Department of Health. Studies in the Florida Everglades have consistently shown concentrations of Hg in fish exceeding health-based standards (Atkeson, 1999).

Hg in water bodies can be attributed to either deposition of Hg from the air or the direct discharge of Hg-laden wastewater. Stormwater runoff may carry Hg that has deposited on the ground into bodies of water. 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 ppt (NACWA, 2002). If this standard is extended throughout the country, Hg emissions from a variety of sources would need to be greatly reduced.

The 2005 U.S. Clean Air Mercury Rule mandates controls of Hg released by electric power generators, a major global source of atmospheric Hg. These controls are projected to cost nearly \$1 billion annually by 2020 (US-EPA, 2005). However, despite these projected high costs, the potential benefits resulting from reduced emissions remain uncertain, unless a parallel effort addresses the issue of Hg removal from wastewater effluents and discharges into natural aquatic systems.

Traditional technologies for Hg removal, such as activated carbon, may be limited in their effectiveness for wastewaters with changing characteristics. These sorbents have specific adsorption capacities and must be disposed of when these are exceeded, thus transferring a liquid-phase pollution problem to a solid waste problem. A robust technology that can treat waters of various characteristics and can be regenerated is needed.

Materials and Methods

Experiments began with 100 $\mu\text{g/L}$ Hg solutions prepared with a concentrated $\text{Hg}(\text{NO}_3)_2$ stock solution and deionized water (18.2 M Ω -cm) or effluent from the

University of Florida's Water Reclamation Facility. Batch experiments were carried out in a 100 mL capacity cylindrical batch reactor that was stirred magnetically. A UV bulb (U-tube 254 nm 8W) was inserted directly into the batch solution and was left off for adsorption alone experiments or illuminated for photocatalysis reactions. Column studies were performed in a cylindrical reactor with a quartz sleeve through the center, which housed a UV bulb (12" 254 nm 13 W). Aqueous solutions were pumped through the column at a controlled flowrate with a peristaltic pump and PTFE tubing. STC materials were prepared in 3 different size fractions, cylindrical STC pellets of approximately 3 mm in diameter and 5 mm in length, and ground and sieved STC of 45 – 90 μm or 6 – 45 μm in primary particle size. STC pellets were used in a packed bed in the column studies while the ground and sieved STCs were used in the batch studies. All results are presented as the final mercury concentration over the initial mercury concentration. Error bars represent the range of duplicate experiments.

Results and Discussion

Various STC formulations were tested in the batch reactor beginning with the 45 – 90 μm primary particle size fractions and mercury-deionized water solutions. As TiO_2 loading increased from 0% to 4% to 32% in the smallest pore size STC (targeted for 30 Å in diameter), so did Hg removal under adsorption alone, reaching over 90% removal at 60 minutes for the 30 Å 32% STC. Removal profiles were very similar for 30 Å 4% and 30 Å 32% with saturation reached in 30 minutes. At the largest TiO_2 loading (32%), a comparison of pore size revealed that the largest pore size material (targeted for 320 Å in diameter) removed mercury faster resulting in saturation at 15 minutes and a final mercury removal over 95% at 60 minutes. Therefore, it was determined that the optimal STC formulation for adsorption alone in the 45 – 90 μm fractions was 320A 32%. However, once the primary particle size was reduced to 6 -45 μm , both 30 Å 4% and 320 Å 32% achieved very similar mercury removal trends with greater than 90% mercury removal in 5 minutes. It was concluded that mercury adsorption is dependent on the readily accessible TiO_2 sites on the STC which is improved with increased TiO_2 loading for larger particles and overall by a decrease in primary particle size.

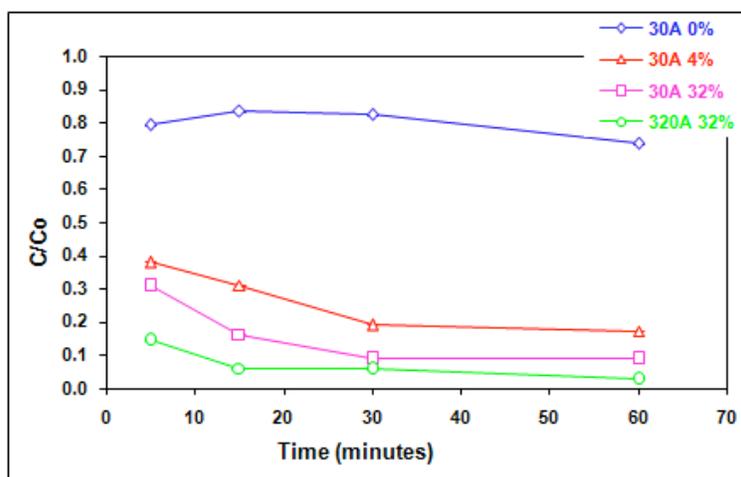


Figure 1: Batch mercury removal from synthetic solutions via adsorption alone, 45 – 90 μm size fractions STC

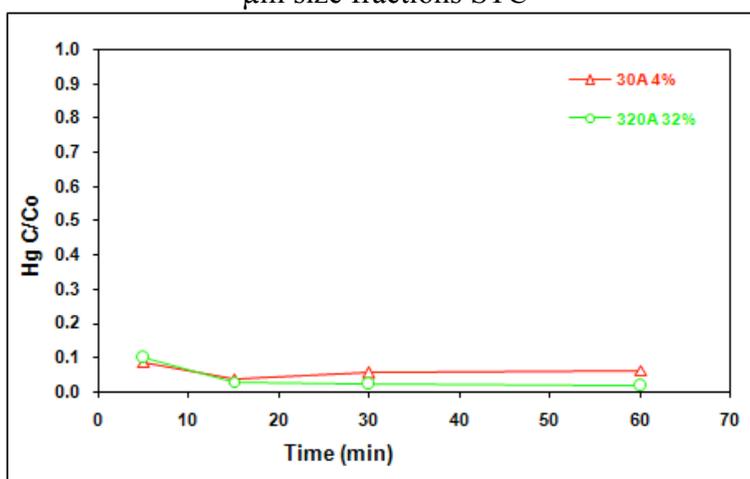


Figure 2: Batch mercury removal from synthetic solutions via adsorption alone, 6 – 45 μm size fractions STC

Following batch adsorption only studies, the same experiments were repeated with UV illumination. Beginning with the small pore size, as TiO_2 loading increased, so did mercury removal. The trend was very similar to adsorption alone for 30 Å 0% and 30 Å 32% without any further improvements, but not for 30 Å 4%. At this TiO_2 loading, performance actually decreased in comparison to adsorption alone. This trend was noted for all pore sizes. Additionally, the smaller size fractions of 6 - 45 μm STC were tested with UV illumination. Again, as in adsorption alone, the smaller size fraction of both the 30 Å 4% and the 320 Å 32% STCs removed mercury faster and to a greater extent than the larger size fractions. In summary, UV illumination did not improve mercury removal for any STC formulation in the mercury-deionized water solutions.

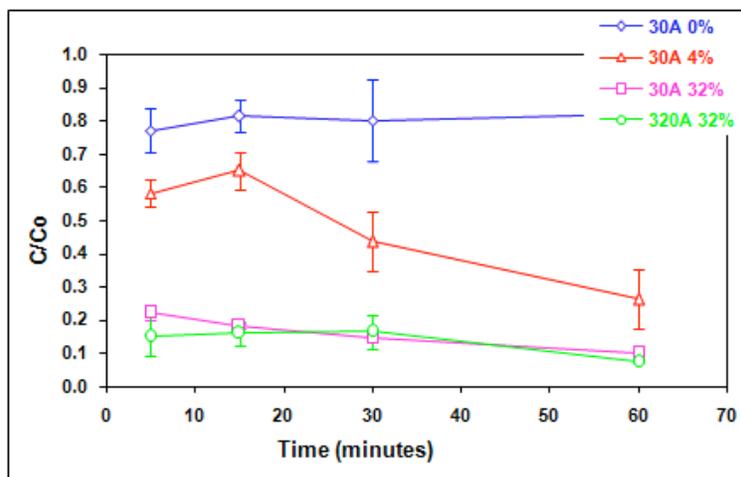


Figure 3: Batch mercury removal from synthetic solutions via photocatalysis, 45 – 90 μm size fractions STC

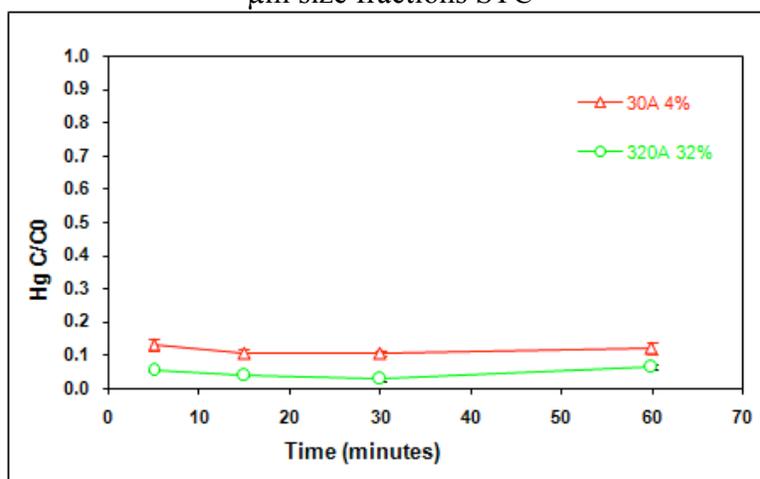


Figure 4: Batch mercury removal from synthetic solutions via photocatalysis, 6 – 45 μm size fractions STC

Based off of results from the batch studies, two column tests were performed to test the feasibility of the column configuration. The optimal parameters selected were: adsorption alone, 320 \AA 32%, and a 20 minute residence time. After a desired volume of mercury solution had been tested, a 5% HCl acid rinse was introduced to the column to regenerate the pellets and an additional run was performed. On the first run, 320 \AA 32% STC achieved about 65% mercury removal. Due to the larger primary particle size of the STC, a reduction in mercury removal was seen from the batch studies. The second run, after regeneration which removed approximately 87% of the sorbed mercury, resulted in about 45% mercury removal. A second column study was performed with a faster residence time of 2.5 minutes to test larger flow volumes. This study did not achieve significant mercury removal.

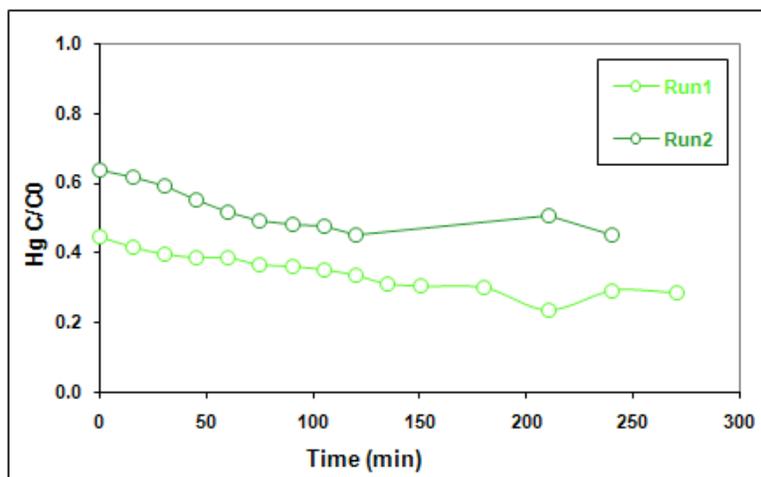


Figure 5: Continuous flow mercury removal from synthetic solutions via adsorption alone, pellet size fraction 320 Å 32% STC, 20 minute residence time

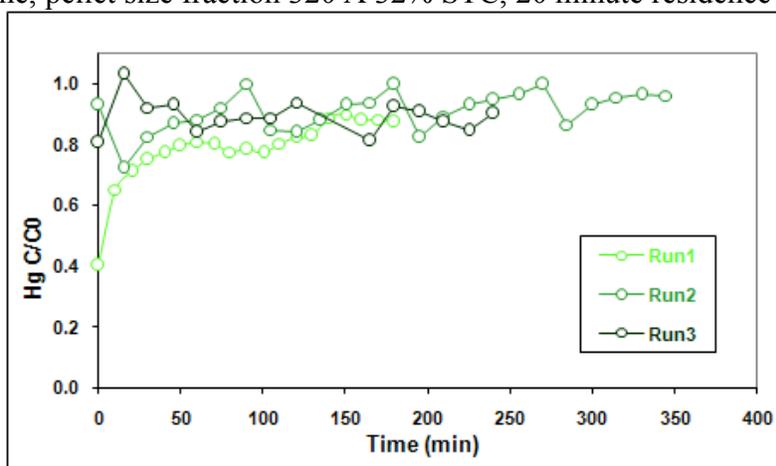


Figure 6: Continuous flow mercury removal from synthetic solutions via adsorption alone, pellet size fraction 320 Å 32% STC, 2.5 minute residence time

Additionally, testing was performed with water from the UF Water Reclamation Facility to present a real life water chemistry aspect. It was hypothesized that in these studies, different trends with respect to adsorption alone versus photocatalysis may be realized due to the organic compounds contribution. Both the worst performing STC (30 Å 4%) and the best (320 Å 32%) were tested under adsorption alone and photocatalysis in the batch configuration. Mercury removal from the UF Water Reclamation Facility reached 75% with the 320 Å 32% STC after 30 minutes (Figure 7). The result of adding competitive ions to the water chemistry was a reduction in mercury removal by 20% from that of the mercury-deionized water solutions. Photocatalysis, on the other hand, did not achieve mercury removal for either STC formulation (Figure 8). This was contrary to expected and would need further research to understand the phenomena.

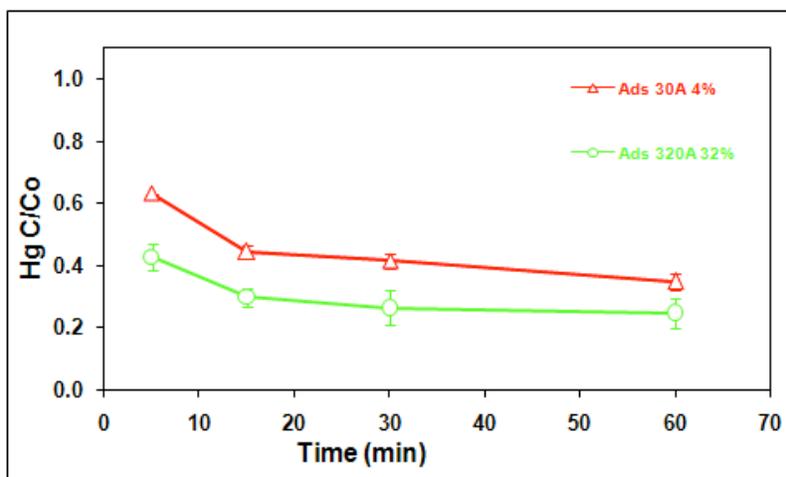


Figure 7: Mercury removal from UF Water Reclamation Facility via adsorption, 45 – 90 μm size fractions STC

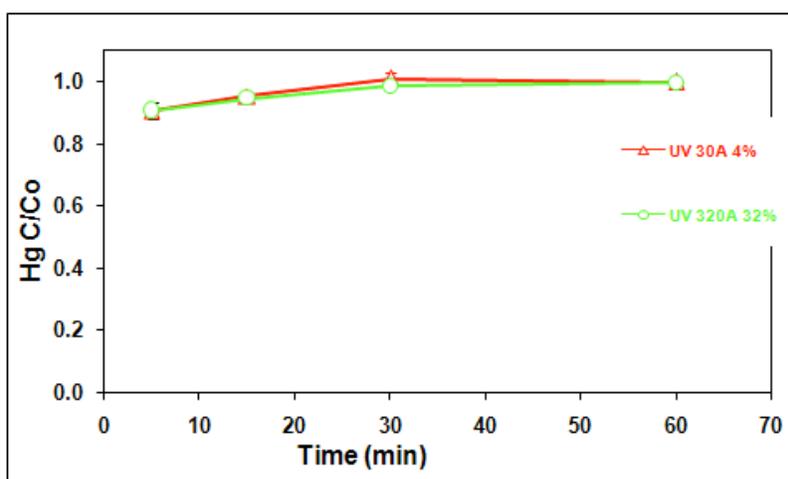


Figure 8: Mercury removal from UF Water Reclamation Facility via photocatalysis, 45 – 90 μm size fractions STC

Also investigated was mercury adsorption onto calcium sulfate (CaSO_4), a byproduct of the flue gas desulfurization (FGD) wet-scrubber technology installed for sulfur dioxide (SO_2) removal in the coal fired power industry. Adsorption experiments were performed in 60 mL bottles with 40 mL of various mercury (from HgCl_2) concentrations, with a 0.01 M NaCl background electrolyte concentration, and CaSO_4 solid for 24 hours on a shaking table. As CaSO_4 mass loading increased, the fraction of mercury adsorbed also increased. While the amount of mercury adsorbed increased with increased initial mercury concentration, the fraction of mercury adsorbed decreased.

Overall, the quantity of mercury removed from the aqueous system was very small. Based on the highest adsorption fraction, only 0.09 mg/L would be extracted in a TCLP or SPLP. The regulatory limit for mercury TCLP is 0.2 mg/L. Therefore, there would be no risk of mercury contamination from the CaSO₄ material.

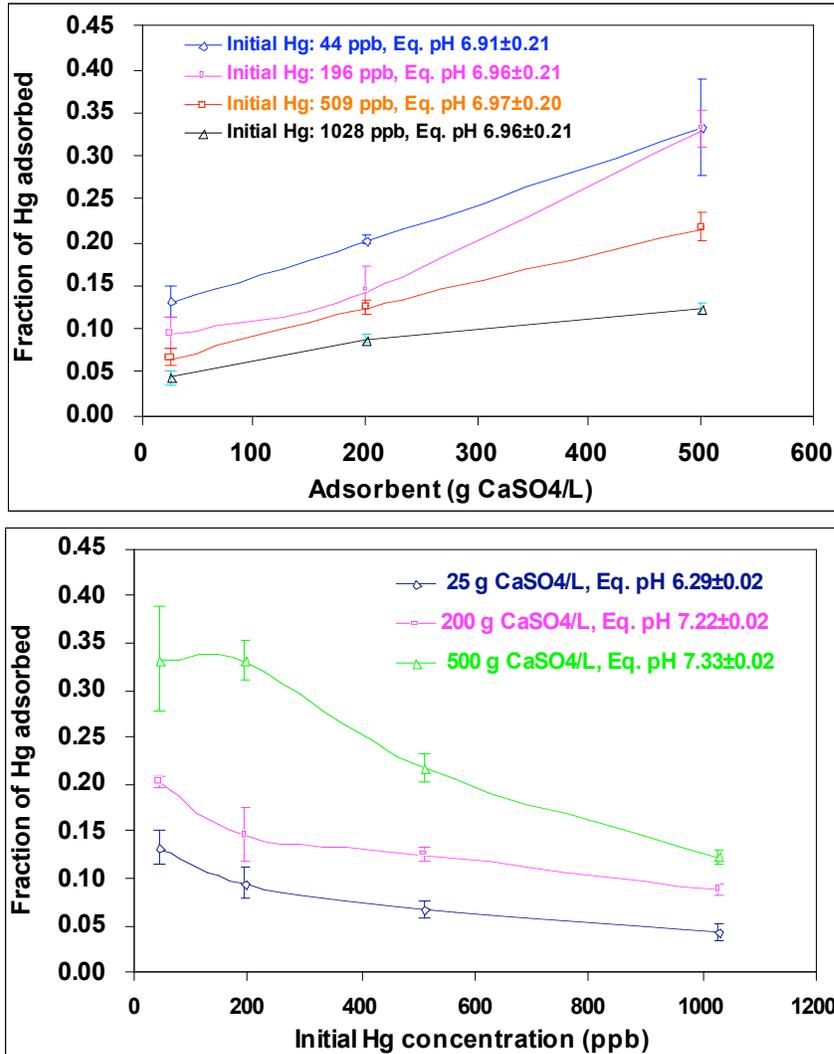


Figure 9: Mercury adsorbed dependent upon initial mercury solution concentration and calcium sulfate mass loading

Conclusions

In conclusion, STCs are capable of reducing mercury concentrations in low level mercury solutions. The most effective use of the STC would be in a slurry batch reactor utilizing 320 Å 32% STC under adsorption alone. Studied here, mercury removal with this material reached between 75% and 90% in water reclamation facility effluent and deionized

water solutions respectively. The spent material could then be regenerated with dilute hydrochloric acid or disposed of in a landfill without threat to the environment.

Future Studies

Upon completion of the project described herein, further support will be required for technology development. Along this path, even lower concentrations of mercury need to be studied aimed for mercury removal technology development for a number of wastewaters within the coal-fired power and other industries to achieve a mercury concentration below 10 ppt. There is a strong need for Hg removal from FGD scrubber water to achieve concentrations between 1 and 10 ppt. Thus the focus herein will be on Hg removal from FGD scrubber water from several power plants using STC.

Planned Proposals based on Water Institute Funding

“Photochemical process for removal of Hg and Selenium to below 12 ppt” will be submitted to (Deadline Sept. 15, 2008):

The **Environmental Engineering** program supports fundamental research and educational activities across the broad field it serves, with the goal of applying engineering principles to understand and reduce adverse effects of solid, liquid, and gaseous discharges into land, inland and coastal waters, and air that result from human activity and that impair the ecological and economic value of those resources. It fosters cutting-edge research based on fundamental science and four types of engineering tools - measurement, analysis, synthesis, and design. Proposals emphasizing enhancement of American Competitiveness are encouraged.

Major areas of interest and activity in the program include:

1. Developing innovative biological, chemical, and physical treatment processes to remove and degrade pollutants from water and air
2. Measuring, modeling, and predicting the movement and fate of pollutants in the environment

Developing and evaluating techniques to clean up polluted sites, such as landfills and contaminated aquifers, restore the quality of polluted water, air, and land resources and

rehabilitate degraded ecosystems

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