Removal of trace level aqueous mercury by adsorption and photocatalysis on silica–titania composites

Heather E. Byrne, David W. Mazyck*

Department of Environmental Engineering Sciences, University of Florida, Gainesville, FL, United States

ABSTRACT

Silica–titania composites (STCs) were applied to trace level mercury solutions (100 μg/L Hg) to determine the degree of mercury removal that could be accomplished via adsorption and photocatalysis. STCs are a porous, high surface area silica substrate (>200 m^2/g), manufactured using sol–gel methodology, impregnated with TiO$_2$ nanoparticles. The performance of this material along with its precursors, silica and Degussa P25 TiO$_2$ were compared. Under adsorption alone (no UV illumination), STCs were able to achieve approximately 90% removal of mercury, which is comparable to that of Degussa P25. Silica without TiO$_2$ performed poorly in comparison and was minimally affected by UV illumination. Contrary to expectations, the performance of Degussa P25 was not largely changed by UV irradiation and the STC was detrimentally affected under the same conditions. It was concluded that elemental mercury was formed under UV irradiation with or without the presence of TiO$_2$ due to photochemical reactions, decreasing the mercury removal by STC. Additionally, the primary particle size of the STC was reduced to increase mass transfer. The result was improved Hg removal under adsorption and photocatalysis conditions. Improved adsorption kinetics were also achieved by altering the STC pore size and TiO$_2$ loading.

Published by Elsevier B.V.

1. Introduction

In the late 1950s, the Minamata tragedy alerted the world to the danger of mercury pollution to human health. Human exposure through fish consumption and inhalation of mercury vapor are of increasing concern as many fisheries have become contaminated with varying levels of mercury. Adverse health effects from mercury exposure include an array of neurological dysfunctions which have more drastic effects on sensitive populations and developing children [1,2]. Governments around the world have adopted seafood consumption advisories and recommended safety levels of fish consumption to protect the populations from mercury poisoning [3]. Therefore, it is clear that to meet advisory levels and protect human health and the environment, mercury pollution needs to be controlled.

A promising treatment method for aqueous mercury removal is semiconductor photocatalysis on TiO$_2$ [4–8]. In these studies, mercury removal was achieved through the reduction of divalent mercury species to elemental via reactions with the photogenerated TiO$_2$ electrons. Little to no mercury removal occurred in the presence of UV with the absence of TiO$_2$ [6,8]. In TiO$_2$ solutions, mercury removal was further increased by the addition of an organic scavenger, such as citrate, formic acid, or methanol, which reduced the fraction of e$^-$/h$^+$ pair recombination. Over 95% mercury removal could be achieved beginning with initial concentrations of 100 mg/L of Hg. However, mercury removal at trace levels, ca. 100 μg/L Hg, was not studied. Considering current mercury regulations and health concerns, the occurrence of mg/L Hg waste streams is rare and sub 10 μg/L Hg concentrations are desired in the environment. Such low levels are currently enforced in the Great Lakes region [9]. Therefore, to address present day and future mercury management needs, this study focuses on trace level mercury removal.

Additionally, while TiO$_2$ is an efficient photocatalyst, commercialization of full-scale reactors utilizing nanoparticles, such as TiO$_2$, are limited by the separation of the particles from the waste stream [10]. To overcome this constraint, TiO$_2$ can be immobilized in a substrate such as silica. Silica–titania composites have been used for many applications in semiconductor photocatalysis [11–13]. While titania particles act as a photocatalytic center, silica gel provides a transparent macrosupport for the nanosized titania, enabling tailorable particle size for reduced filtering requirements, and increased surface area (>200 m^2/g) for greater adsorption capacity for many applications. As semiconductor photocatalysis was found to be a promising mercury removal technology via TiO$_2$, it was expected that the application of silica–titania composites would further enhance the removal capabilities.

* Corresponding author at: 312 A.P. Black Hall, P.O. Box 116450, University of Florida, Gainesville, FL 32611. Tel.: +1 352 846 1039; fax: +1 352 392 3076.
E-mail address: dmazyck@ufl.edu (D.W. Mazyck).

The proposed technology can be adapted for various treatment stream applications such as in line, batch, or pump and treat configurations. The silica–titania composite materials have been developed [14], characterized [15], and successfully applied for specific applications for mercury removal from flue gas [14,16], mercury recovery from caustic exhaust emitted from the chlor-alkali industry [17], and the degradation of volatile organic compounds in gas emitted from pulp and paper mills [18]. The aim of this study is to evaluate the potential for silica–titania composites to remove trace level mercury from aqueous solutions.

2. Experimental

2.1. Chemicals and materials

All reagents used in this work were of analytical grade and were used without further purification. Silica–titania composites were produced with a sol–gel method detailed in previous work [14]. Ingredients included tetraethylorthosilicate (TEOS, Fisher reagent grade), ethanol (Fisher, 200 proof), Nanopure water, 1 mol/L nitric acid (diluted from concentrated Fisher, certified ACS), 3 wt% hydrofluoric acid (diluted from 49% Fisher, certified ACS), and Degussa P25 TiO_2. Pore size was modified by altering the quantity of hydrofluoric acid added to the mixture during synthesis while the other ingredients were held constant. Additionally, the mass of Degussa P25 TiO_2 added to the liquid precursors was altered to change the TiO_2 loading. Silica gels were created in the same manner without the addition of TiO_2. Nomenclature for the STCs and silicas is based on the volume ratio of 3 wt% HF to 1 M nitric acid. Subsequent, the STCs are also differentiated by the mass ratio of TiO_2 to STC. For example, STC-1-50 represents a STC with 1 mL of 3 wt% HF to 1 mL of 1 M nitric acid and 50 mg of TiO_2 per 100 mg of dry composite. After all chemical additions, the liquid sol was mixed in a sealed 250 mL polymethylpentene container until gelation occurred creating silica or STC monoliths. Following gelation, the STCs were aged for 48 h in the same container then dried using previously described procedures [14]. Samples were then ground using a mortar and pestle, wet sieved and dried to achieve a particle size distribution from 45 to 90 μm. This fraction, unless stated otherwise, was used for all analyses. Mercury solutions prepared with deionized water and the desired aliquot of $Hg(NO_3)_2$ from Fisher Scientific. Solution pH after the addition of the media was approximately pH 4. No pH adjustments were made.

BET surface areas and average pore size (using the Kelvin equation) of the specific media synthesized for this study were measured on a Quantachrome NOVA 1200 Gas Sorption Analyzer. Samples were outgassed for 12 h at 110 °C prior to analysis.

2.2. Batch testing procedures

Since mercury is a difficult chemical to analyze at low levels [19], due care was taken in all sampling procedures. All vessels for storing mercury solutions or mercury 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. Mercury concentrations were determined using an atomic adsorption spectrometer (Teledyne Leeman Labs) per EPA standard method 254.3.

Batch experiments were carried out in a cylindrical reactor which contacted the mercury solution with the selected media, suspended by magnetic stirring, and a PL-S Twin Tube Short Compact Fluorescent Lamp of 254 nm (bulbs.com, Worcester, MA) (Fig. 1). Media loading was selected to be 1 g/L based on preliminary testing. Silica and STCs were applied as synthesized at a particle size
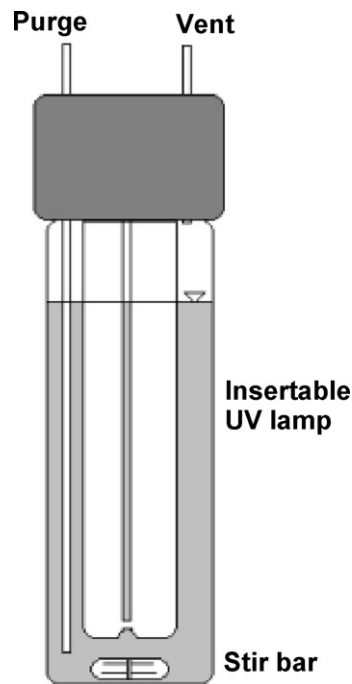

Fig. 1. Schematic of the batch reactor used for adsorption alone and photocatalysis studies.

distribution from 45 to 90 μm while TiO_2 was applied as received from the manufacturer. The reactor was also equipped with a glass purge tube and a glass vent port for in situ purging experiments. The purge was only used for the in situ purging experiments and for all others the 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 min with the UV bulb illuminated (UV photocatalysis) or turned off (adsorption alone in the absence of light). After the desired time elapsed, the solutions were filtered with a 0.45 μm mixed cellulose membrane filter to separate the media. Control samples were also filtered. The filtrate was sampled and analyzed for mercury. Mercury 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.

3. Results and discussion

3.1. STC

The BET characterization of the media discretely prepared and used in this study is presented in Table 1. The silica and STCs are mesoporous solids with a narrow pore size distribution. Average pore diameters were 37, 109, and 232 Å for silica-0.25/STC-0.25, silica-1/STC-1, and silica-2/STC-2 respectively. Alternatively, TiO_2 is a nonporous solid with a low specific surface area of 49 m^2/g. As expected of a composite material of this nature, increasing mass loadings of TiO_2 visibly decreased the specific surface area and pore volume of the STC. Pore diameters are less affected by TiO_2 loading. Also impacted was the availability of TiO_2. While some TiO_2 is unavailable to surface reactions due to internalization in the silica matrix, the available TiO_2 surface area on the STCs is directly related to the mass loading of TiO_2 added during synthesis and would therefore increase with increased TiO_2 mass in the STC. The effect of these changes will be discussed with regards to mercury removal later in this work. Further material characterization can be found elsewhere [15].

Table 1
BET specific surface area, pore diameter and pore volume values as measured by nitrogen adsorption/desorption.

Material	Surface area (m^2/g)	Pore diameter (Å)	Pore volume (cm^3/g)
Silica-0.25	764	33	0.634
STC-0.25-12	796	33	0.654
STC-0.25-30	655	36	0.591
STC-0.25-50	441	46	0.506
Silica-1	467	116	1.351
STC-1-12	398	101	1.008
STC-1-30	358	112	1.006
STC-1-50	271	107	0.725
Silica-2	236	265	1.565
STC-2-12	223	250	1.397
STC-2-30	192	244	1.176
STC-2-50	200	169	0.843
Degussa P25 TiO_2	49	–	–

*Standard error ± 5%.
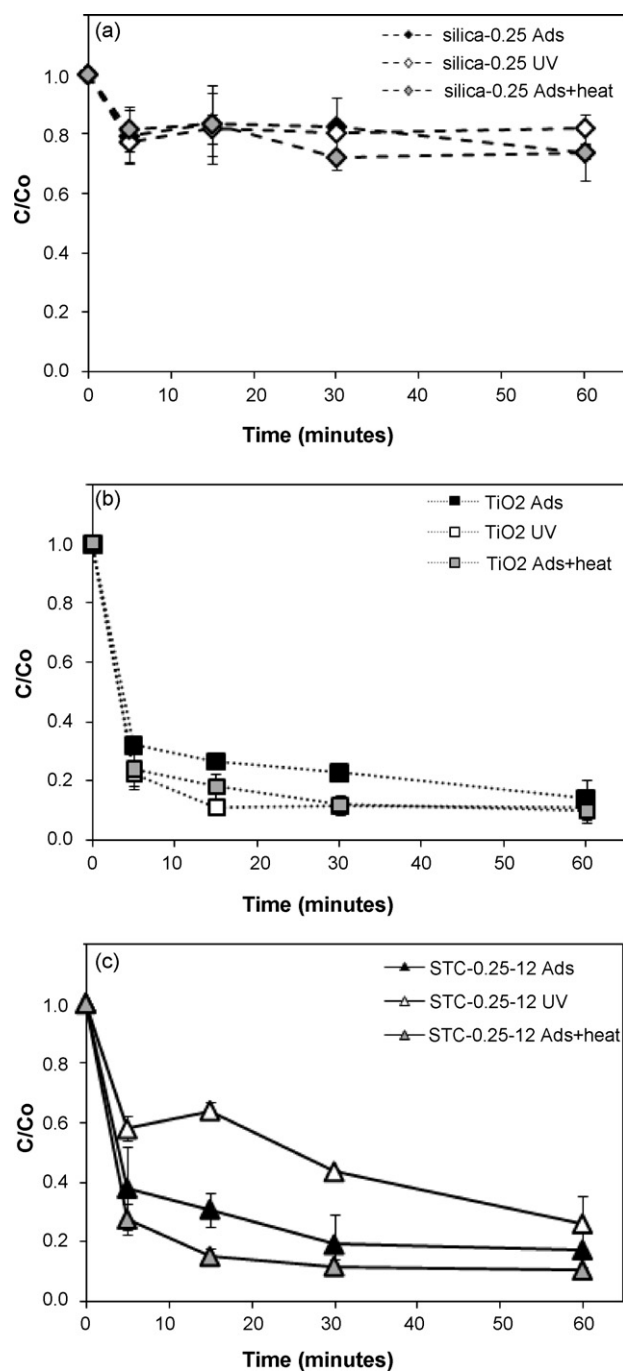
3.2. Mercury removal

3.2.1. Adsorption

The removal of mercury from 100 μg/L aqueous solutions by STC-0.25-12 was compared with that of its parent compounds, Degussa P25 TiO_2 and silica-0.25. Equal mass loadings, 1 g media/L solution, of each material were used for the comparison. STC-0.25-12 was selected as a starting point for testing based on successful applications of this material in the past with other contaminants. Of the STC formulations, STC-0.25-12 possesses the highest specific surface area which is usually correlated with contaminant removal. Under adsorption alone (Fig. 2, black filled markers), silica does not have a large affinity for mercury. However, once TiO_2 is added to create a STC, mercury removal sharply increases. STC-0.25-12 performs very similarly to the benchmark Degussa P25 TiO_2. The mercury concentration is significantly lowered within only 5 min and additional adsorption continues slowly up to 60 min which is where pseudo steady state was determined to be achieved. These results indicated that STCs are a very promising sorbent for mercury removal.

3.2.2. Photocatalysis

It was expected, based on previous literature researching higher concentrations of mercury [4–8], that mercury removal under photocatalysis conditions involving TiO_2 would be even greater. Once irradiated with UV, the TiO_2 and STC system performed unexpectedly (Fig. 2, open markers). The silica-0.25 did however perform as anticipated; its mercury removal did not deviate from adsorption alone conditions since it did not contain any photocatalytic materials. While further mercury removal via TiO_2 photocatalysis in the presence of UV was predicted, mercury 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 hindered under UV irradiation until greater contact times (60 min).

3.2.3. 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 mercury solution. Therefore, the effect of increased solution temperature on mercury 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 (Fig. 2, gray filled markers). The heat profile was achieved using the adsorption set-up on a heated stir plate to

Fig. 2. Mercury removal onto (a) silica-0.25, (b) TiO_2, and (c) STC-0.25-12 via adsorption alone (Ads), adsorption in the dark at elevated temperatures (Ads + heat) and UV photocatalysis (UV).

increase the temperature slowly over time (an increase of about 20 °C over 60 min). STC-0.25-12 and TiO_2, in the absence of UV but with an elevated solution temperature to mimic the temperature of the solution in the presence of UV, again performed very similarly to each other (Fig. 2b and c) as in the original adsorption alone results. Specifically, mercury removal by TiO_2 under increased solution temperature mimicked that of UV indicating that photocatalysis did not contribute to mercury removal. Silica-0.25 was minimally impacted by the change in conditions.

Mercury removal by each material was compared to the reactor conditions. Mercury removal by silica-0.25 remained unchanged as experimental conditions changed (Fig. 2a). TiO_2 exhibited a
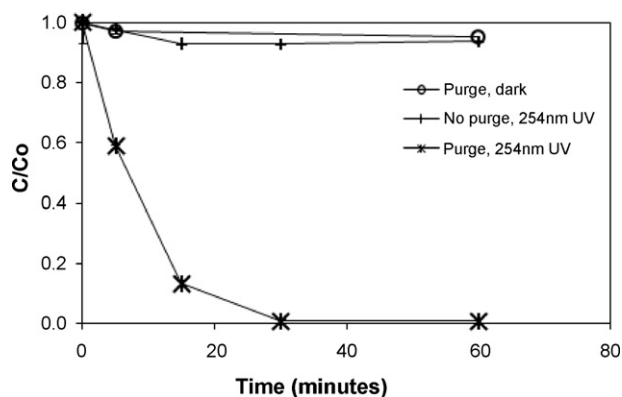
Fig. 3. Mercury reduction by UV (254 nm) and removal by nitrogen purge.

Fig. 4. Comparison of different primary particle sizes of STC-0.5-12 for removal via adsorption and photocatalysis.

slight improvement in mercury removal under 60 min for the UV and adsorption at elevated temperatures compared to adsorption alone (Fig. 2b). However, once 60 min is reached, the same mercury removal is attained. Therefore, photochemical reactions are ineffective for mercury removal beyond that of adsorption at these trace concentrations. On the contrary to the results for silica-0.25 and TiO_2, it can be confirmed that mercury removal under UV irradiation is distinctively less than that by adsorption and adsorption with elevated temperatures (Fig. 2c) until 60 min is reached. Here it is evident that the negative change in mercury removal by STC-0.25-12 under photocatalysis is caused by UV irradiation alone and not a change in temperature.

3.3. Effect of UV on adsorbent

While STC-0.25-12, exhibited a delay in mercury removal in the presence of UV irradiation as compared to in the dark, this phenomenon was not seen with the individual silica-0.25 or TiO_2 materials. Under 254 nm UV light, TiO_2 will be photoactive and generate e^-/h^+ pairs. Mercury removal by TiO_2 in this work was not affected by the presence (photocatalysis system), or absence (adsorption with heat) of these processes. The affinity of mercury for silica was also unchanged as silica is not reactive under the presence of UV [20,21]. Therefore, the effect of UV on the adsorbate was considered to be the significant factor causing a reduced mercury removal at times less than 30 min.

3.4. Effect of UV on adsorbate

Photochemical reactions of mercury due to the presence of sunlight have been gaining attention as of late [23]. Therefore, it was desirable to investigate the effect of mercury speciation under UV illumination without a photocatalyst to further isolate the changes responsible for a decreased mercury removal for shorter contact times in the UV STC system. For these studies, the same batch reactor was used without media. Mercury 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 mercury or contribute to any redox reactions in the presence of UV. A control study without UV was performed to ensure that there was no mercury loss due to purging alone. Another control with UV but no purge was also performed to ensure there was no mercury loss due to UV without a purge. The results in Fig. 3 show that the controls, with either a purge or UV, did not remove appreciable quantities of mercury in agreement with high level mercury photocatalysis experiments [6,8]. However, in the presence of both the purge and UV irradiation, mercury con-
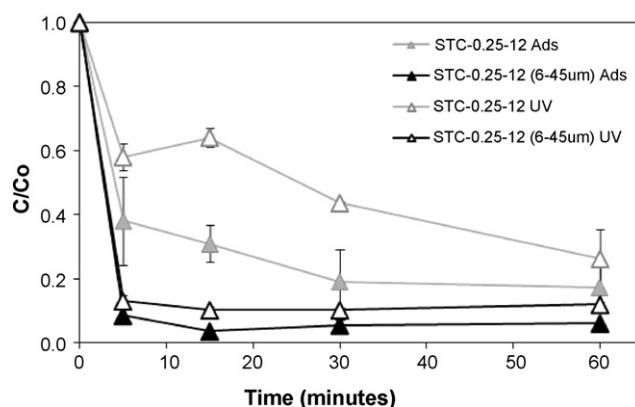
centrations diminished substantially. Trace level aqueous divalent mercury (the dominant species in an aqueous solution of mercury nitrate) could indeed be reduced to elemental mercury in the presence of UV and be volatilized into the nitrogen stream and removed from solution. As further verification that volatilization occurred, no filterable species of mercury greater than 0.45 μm were found.

Since elemental mercury can be produced by photochemical reactions in the absence of TiO_2, the speciation change will occur in all solutions irradiated by UV light even before contacting the photocatalyst. As an additional test, a mercury solution was irradiated with UV followed by an immediate nitrogen purge once the light was extinguished. This resulted in little to no mercury removal from solution. Although mercury 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 mercury occur in solution. TiO_2, being of nanosize and a photocatalyst, will adsorb UV and likely decrease the reduction reactions of mercury in solution promoting more oxidized mercury in solution. In addition, due to its size, TiO_2 will have more interactions with mercury, which can lead to adsorption, over much larger micron particles during a given contact time. Due to these properties, the removal of mercury by TiO_2 is not impacted by the presence or absence of UV light at low concentration of mercury. The removal of mercury by STC-0.25-12, with a larger particle size than TiO_2 and a lower photocatalyst (TiO_2) surface area to absorb UV photons, is negatively impacted by the presence of elemental mercury.

3.5. Effect of primary particle size

Since mercury 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 above, 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 primary particle sizes of 6–45 μm which were 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 Fig. 2c in Fig. 4.

Decreased particle size increased mercury removal under 30 min. Mercury removal begins to reach steady state after only 5 min for a size fraction of 6–45 μm versus an hour for 45–90 μm for STC-0.25-12. Additionally, the mercury 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 mercury reduction pho-
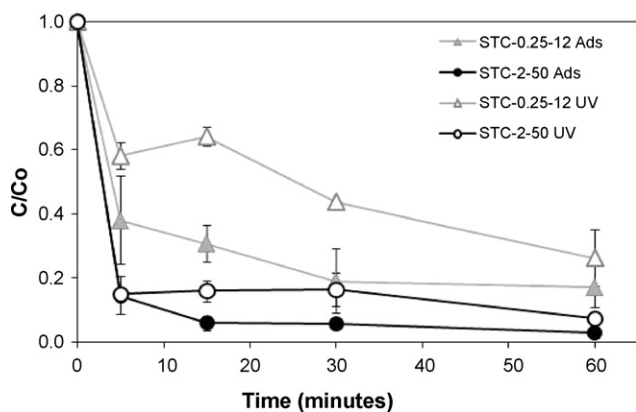
Fig. 5. Comparison of STC-0.25-12 to STC-2-50 for mercury removal via adsorption and photocatalysis.

tochemistry and an increased interaction between adsorbent and adsorbate increased mercury adsorption in a less time than for a larger STC particle.

While decreasing the STC particle size helped elucidate mercury 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 TiO_2 loading to achieve greater mercury removal than with STC-0.25-12.

3.6. Effect of TiO_2 surface area and pore size

Both pore size and TiO_2 loading were increased from previously tested STC-0.25-12 to create STC-2-50. The results of STC-2-50 applied to mercury removal are shown in Fig. 5 and compared to STC-0.25-12 results from Fig. 2c.

By increasing pore size and TiO_2 loading, mercury removal was increased. Other conformations of STC shown in Table 1 were also tested and achieved mercury removals in-between that of STC-0.25-12 and STC-2-50. Comparing the specific surface areas of the two materials (Table 1), STC-2-50 has a much lower specific surface area than STC-0.25-12 but performs better. However, while the total specific surface area of the composite is lower, the specific surface area of TiO_2 in the STC increases with increased TiO_2 loading [15]. STC-2-50 has more available TiO_2 adsorption sites than that of STC-0.25-12. Therefore, mercury removal is dependent upon the fraction of TiO_2 specific surface area in the STC and not the silica specific surface area. It can be concluded that the majority of mercury is adsorbing to the TiO_2. Additionally, STC-2-50 does have a larger average pore diameter than STC-0.25-12 which can increase pore diffusion and therefore a more rapid removal of mercury.

4. Conclusion

Greater than 90% mercury removal can be achieved with STC-2-50 with decreased energy requirements for filtration as compared to TiO_2 alone. The combination of silica and TiO_2 provides a macrosorbent with cation electrostatic attraction to achieve a high degree of trace level aqueous mercury removal by adsorption. Contrary to previous assumptions, photocatalysis of trace level mercury was not more successful than adsorption alone. The production of elemental mercury produced by photochemical reactions caused delayed mercury removal compared to adsorption alone depending on particle size. While this is true of synthetic mercury solutions, the addition of other compounds naturally found in the environment, especially organics, photocatalytic reactions may be advantageous to simultaneously reduce organic matter while removing mercury or to break down mercury compounds that may be difficult to adsorb from solution. Based on the prepared water studies, this technology is promising and should be tested for the treatment of mercury burdened waters such as contaminated groundwaters from industrial activity, effluent from chlor-alkali facilities employing a mercury cell process, flue gas desulfurization liquids and others.

References

[1] U.S. E.P.A., Mercury Study Report to Congress, EPA-425/R-97-006, Office of Air Quality Planning & Standards and Office of Research and Development, 1997.
[2] F. Zahir, S.J. Rizwi, S.K. Haq, R.H. Khan, Low dose mercury toxicity and human health, Environ. Toxicol. Pharmacol. 20 (2005) 351–360.
[3] U.N.E.P. Chemicals, Global mercury assessment, Report no. 54790-01, Geneva, Switzerland, 2002.
[4] N. Serpone, K. Ah-You, T.P. Tran, R. Harris, AM1 simulated sunlight photoreduction and elimination of Hg(II) and CH3Hg(II) chloride salts from aqueous suspensions of titanium dioxide, Sol. Energy 39 (1987) 491–498.
[5] M.A. Aguado, S. Cervera-March, J. Gimenez, Continuous photocatalytic treatment of mercury(II) on titania powders: kinetics and catalyst activity, Chem. Eng. Sci. 50 (1995) 1561–1569.
[6] S.G. Botta, D.J. Rodriguez, A.G. Leyva, M.I. Litter, Features of the transformation of Hg-II by heterogeneous photocatalysis over TiO_2, Catal. Today 76 (2002) 247–258.
[7] L.B. Khalil, M.W. Rophael, W.E. Mourad, The removal of the toxic Hg(II) salts from water by photocatalysis, Appl. Catal. B 36 (2002) 125–130.
[8] X. Wang, S.O. Pehkonen, A.K. Ray, Photocatalytic reduction of Hg(II) on two commercial TiO_2 catalysts, Electrochim. Acta 49 (2004) 1435–1444.
[9] U.S. E.P.A., Water Quality Criterion for the Protection of Human Health: Methylmercury, EPA-823-R-01-001, Office of Science and Technology and Office of Water, 2001.
[10] J. Aguado, R. van Grieken, M. Lopex-Munoz, J. Marugan, A comprehensive study of the synthesis, characterization and activity of TiO_2 and mixed TiO_2/SiO_2 photocatalysts, Appl. Catal. A 312 (2006) 202–212.
[11] C. Anderson, A.J. Bard, Improved photocatalytic activity and characterization of mixed TiO_2/SiO_2 and TiO_2/Al_2O_3 materials, J. Phys. Chem. B 101 (1997) 2611–2616.
[12] K.Y. Jung, S.B. Park, Enhanced photoactivity of silica-embedded titania particles prepared by sol–gel process for the decomposition of trichloroethylene, Appl. Catal. B 25 (2000) 249–256.
[13] P. Pucher, M. Benmami, R. Azouani, G. Krammer, K. Chhor, J.F. Bocquet, A.V. Kanaev, Nano-TiO_2 sols immobilized on porous silica as new efficient photocatalyst, Appl. Catal. A 332 (2007) 297–303.
[14] E. Pitoniak, C.Y. Wu, D. Londeree, D. Mazyck, J.C. Bonzongo, K. Powers, W. Sigmund, Nanostructured silica-gel doped with TiO_2 for mercury vapor control, J. Nanopart. Res. 5 (2003) 281–292.
[15] H.E. Byrne, W.L. Kostedt, J.M. Stokke, D.W. Mazyck, Characterization of HF-catalyzed silica gels doped with Degussa P25 titanium dioxide, J. Non-Cryst. Solids 355 (2009) 525–530.
[16] E. Pitoniak, C.Y. Wu, D.Q. Mazyck, K.W. Powers, W. Sigmund, Adsorption enhancement mechanisms of silica–titania nanocomposites for elemental mercury vapor removal, Environ. Sci. Technol. 39 (2005) 1269–1274.
[17] J.M. Stokke, D.W. Mazyck, Development of a regenerable system employing silica–titania composites for the recovery of mercury from end-box exhaust at a chlor-alkali facility, J. Air Waste Manage. Assoc. 58 (2008) 530–537.
[18] J.M. Stokke, D.W. Mazyck, C.Y. Wu, R. Sheahan, Photocatalytic oxidation of methanol using silica–titania composites in a packed-bed reactor, Environ. Prog. 25 (2006) 312–318.
[19] J.L. Parker, N.S. Bloom, Preservation and storage techniques for low-level aqueous mercury speciation, Sci. Total Environ. 337 (2005) 253–263.
[20] A. Kanta, R. Sedev, J. Ralston, Thermally and photoinduced changes in the water wettability of low-surface-area silica and titania, Langmuir 21 (2005) 2400–2407.
[21] A. Kanta, R. Sedev, J. Ralston, Preparation of silica-on-titania patterns with a wettability contrast, Langmuir 21 (2005) 5790–5794.
[23] H. Zhang, Photochemical redox reactions of mercury, Struct. Bond. 120 (2006) 37–79.