Advanced Mercury Treatment Technologies: Strategies to Successfully Meet Lower Limits

by Scott A. Grieco

Whether we like it or not, mercury is still an important component of many industrial and consumer products including dental fillings, electric switches, thermostats, batteries, fluorescent lamps, and chemicals. In addition to direct industrial and consumer connections, it has been documented that a portion of environmental mercury concentrations are occurring through atmospheric deposition.[1] Despite increased environmental stewardship of mercury, the fact that we still use it means that we must continue mitigating the release from active wastewater discharges, and remediate surface and ground water supplies from past activities.

In the Spring 2006 edition of *Clearwaters,* Sandra Lizlovs described the latest focus on both lower analytical detection and discharge limits.[2] New York State has adopted a 200 ng/L (nanogram per liter) discharge limit, with the ultimate goal to be even lower. As an idea of where this may be going, Michigan has adopted a discharge limit of 10 ng/L for mercury.

How do we successfully achieve these extremely low discharge limits? The answer comes from advancements in our understanding of surface chemistry, nanotechnology and biology. The mercury treatment technologies presented below can be defined in three main categories: adsorption, co-precipitation, and phytoremediation. The remainder of this article describes specific technologies and, where applicable, provides real-world results of mercury treatment.

Adsorption

Adsorption is a process of accumulating mercury on the surface of a solid. For low-level mercury treatment, potential adsorption processes include: sulfur-impregnated granular activated carbon (SGAC); selective ion exchange resins (IX); Forager® Sponge; and, self-assembled mercaptan on mesoporous silica (SAMMS). Although differing significantly in the solid material chemistry and technical approach to the adsorption, there are some similarities common to each of these adsorption processes. Adsorption is typically most appropriate for ionic forms of dissolved mercury. For full-scale applications, the adsorbent material is usually placed in a closed vessel called a packed-bed contactor. Because these contactors can plug with solids, solids removal through settling or filtration may be required upstream of the packed-bed contactor. This approach extends the operational life of the contactor, minimizing backwashing of the adsorbent medium in the packed-bed contactor, and increasing the overall quantity of wastewater requiring treatment. The quantity of the adsorbent required is based on adsorption capacity (mass of mercury per mass of adsorbent – mg/g (milligram per gram). Typically, simple bench-scale isotherm or small column tests are performed to assess the adsorption capacity and quantify the amount of adsorbent required.

SGAC is a special form of granular activated carbon. Although granular activated carbon has an affinity to adsorb mercury, the adsorption capacity is relatively low. By impregnating the granular activated carbon with a compound that will chemically react with the mercury, the adsorption capacity is increased. Sulfur provides a mechanism to bind the mercury through formation of mercuric sulfide (HgS), which is a very stable and tightly bonded insoluble material. As an example of performance, a two-stage SGAC contactor treating groundwater removed mercury from 1,500 ng/L to 80 ng/L in the first stage, and achieved 2.5 ng/L after the second stage. The cost of SGAC media is approximately $200 per cubic foot ($ft^3$). Additionally, it should be noted that SGAC cannot be regenerated, so once used it must be disposed of and replaced with fresh SGAC.

Selective ion exchange (IX) resins for mercury fall in the category of chelating resins, which can be obtained from several manufacturers. In general, ion exchange resins comprise an inert substrate, which provides the structure to attach the ion exchange functional group. For the case of mercury-specific chelating resins, the substrate is polystyrene and the functional group is an organic thiol-based molecule, which bonds with the mercury and forms an insoluble thiol salt. These resins have a preferential selectivity, with mercury being highly preferred over other heavy metals.[3] However, elevated background concentrations of the lesser-selective compounds (i.e., calcium or sodium) can essentially "blind" the resin and lower or eliminate the selectivity of the resin. In a particular bench-scale isotherm jar test, mercury was removed from 380,000 ng/L to less than (<) 200 ng/L. Other applications have shown effluent concentrations <50 mg/L. The cost of these resins is generally high (greater

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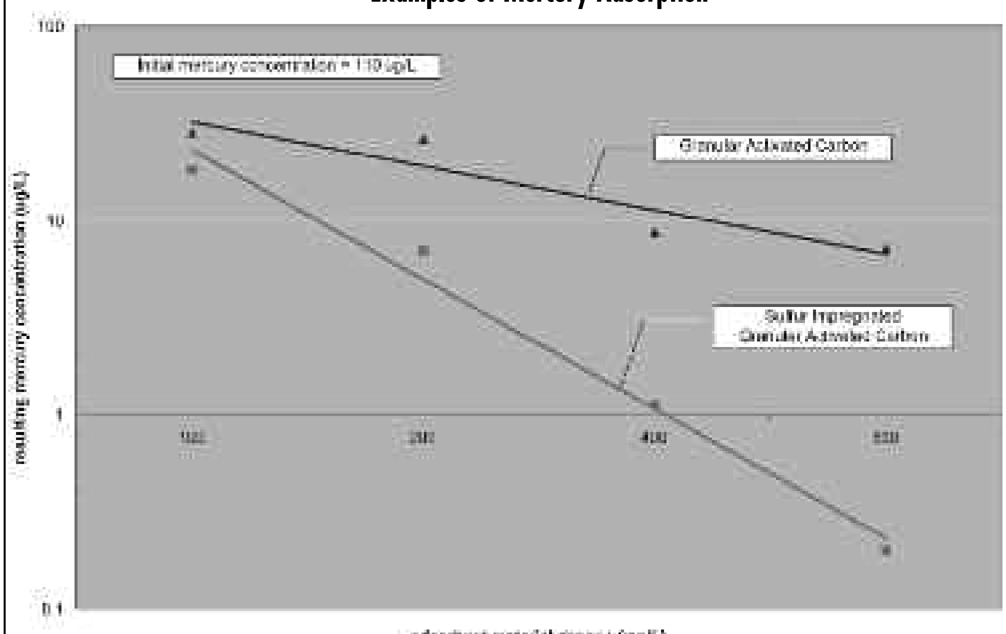
Examples of Mercury Adsorption



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Mercury treatment will typically involve evaluation on the bench scale.

than $400 per ft^3). Additionally, it should be noted that although ion exchange resins can be regenerated, technical constraints, as well as the practicality of managing a liquid mercury backwash wastewater, make regeneration impractical. Therefore, when these resins are exhausted, they are typically disposed of as a solid, and replaced with fresh resin.

The Forager® Sponge is a specific type of adsorption resin developed by Dynephore, Inc.[4] The Forager® Sponge consists of an aliphatic polyamide substrate with a dithiocarbamate functional group. Dynephore claims high selectivity for mercury (three to four times that of ion exchange, and over 10 times that of carbon) and quick kinetics, which results in a smaller unit for equivalent contact time. In a particular bench-scale jar test, results showed mercury removed from 100,000 ng/L to <50 ng/L. Recent quotations on resin costs are approximately $600 per ft^3. It should be noted that the specific sponge type utilized for mercury is not able to be regenerated, and requires disposal once exhausted.

The SAMMS technology is a product of recent advancements in surface chemistry and nanotechnology developed through Pacific Northwest National Laboratories, Inc.[5] The SAMMS product for mercury removal uses a thiol-based functional group. One benefit of this product is that it incorporates a highly engineered substrate structure, which provides an extremely large surface area (approximately 1000 ft^3 per gram of material). This large surface area offers ample sites for exchange; published literature indicates a mercury capacity of up to 635 mg/L. Advantages of this technology, claimed by the manufacturer, include evidence of minimal interference from competing cations (e.g., calcium and sodium) in the wastewater matrix, effectiveness in removing strongly complexed and chelated mercury from aqueous wastes, and the ability to treat wastewater to approximately 10 ng/L. The most recent information from the developer indicates that only research-level quantities (bench-scale or small pilot-scale column) are available, and thus full-scale application is impractical at this time.

Co-precipitation

Co-precipitation is the removal by a precipitate of substances normally soluble under the conditions employed.[6] In the case of mercury treatment, standard precipitation with sodium sulfide produces HgS (mercury sulfide), or sodium hydroxide produces $Hg[OH]_2$ (mercury hydroxide). At elevated pH values, standard precipitation has limits of treatment in the microgram per liter (µg/L) range based on the chemical principles of minimum solubility. Today's limits are much lower than these theoretical sulfide and hydroxide solubilities, which is where co-precipitation proves beneficial. Co-precipitation combines "standard" hydroxide precipitation with additional surface adsorption to an iron or aluminum salt. The advantage of using the aluminum sulfate (alum) or ferric chloride salt is that these constituents act as both a coagulant for "standard" precipitate, as well as a surface adsorbent for the co-precipitation. Typically, co-precipitation is conducted at elevated pH values (eight to 10 SU or standard units). As an example of performance, a full-scale ground water system removes mercury from 250,000 ng/L to 100 ng/L using ferric chloride; bench-scale testing on a surface water treatment removed mercury from 4,000 ng/L to <50 ng/L using alum. The cost for precipitation chemicals is dependent on pH of the wastewater, as well as dosage of treatment chemistry required (usually determined through jar testing). To understand the full economic picture, both capital (chemical metering, solids separation, and solids dewatering) and operational (chemical addition, labor, and solids disposal) costs need to be considered.

Phytoremediation

Phytoremediation is the science of using plants, either natural or genetically engineered, to treat wastewater. Phytoextraction, the main mechanism for mercury treatment, utilizes plants to absorb, uptake, and concentrate mercury into the above-ground biomass. Plant species that have demonstrated successful phytoextraction include penneycress, Indian mustard, alyssum, sunflowers, and hybrid poplars. As an example of performance, an engineered wetland at the Savannah River Site provided more than (>) 80 percent mercury removal, with effluent concentrations less than 0.26 ng/L.[7] This site example was a two-acre wetland area designed for approximately 48 hours detention at an average water depth of 12 inches. Phytoremediation holds promise by providing environmental and aesthetic benefits, and may replace the need for "concrete and steel"

A wetland area can be an instrument for phytoremediation, using nature to treat wastewater.

treatment systems in many instances. Phytoremediation is most appropriate for dilute wastewaters. Because it is generally a passive approach to treatment, it can be argued that the cost of the phytoremediation is lower than that of traditional processes. Items such as the required acreage for treatment; containment of the wetland area; long term viability of plant performance; operation in colder climates; and biomass harvesting methods, need to be evaluated when considering phytoremediation as a potential option.

In summary, mercury resulting from our industrial activities both past and present, is a major environmental concern. Due to bioaccumulation and other factors in the environment/food-chain, ambient water quality standards (AWQS) and corresponding discharge limits are being ratcheted down. Moreover, analytical technology is now in place to allow these low limits to be realized. Therefore, treatment approaches will need to be implemented to achieve these lower limits. This article provided a general overview of several available technologies that can be utilized to achieve these lower limits and some examples of actual performance. As with any technology, it is recommended that the performance of these technologies be evaluated through testing using actual wastewater, because performance, capacities and resulting economics may be different than those presented here or in published reports and sales information.

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Illustration by Michelle Heyes