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TRACE-LEVEL MERCURY REMOVAL FROM SURFACE WATER

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ABSTRACT

Many sorbents have been developed for the removal of mercury and heavy metals from waters; however, most of the data published thus far do not address the removal of mercury to the target levels represented in this project. The application to which these sorbents are targeted for use is the removal of mercury from microgram-per-liter levels to low nanogram-per-liter levels. Sorbents with thiouronium, thiol, amine, sulfur, and proprietary functional groups were selected for these studies.

Mercury was successfully removed from surface water via adsorption onto Ionac SR-4 (Sybron Chemicals, Inc.), Keyle:X (SolmetexX), and Mersorb (Nucon International, Inc.) resins to levels below the target goal of 12 ng/L in batch studies. A thiol-based resin (Ionac SR-4) performed the best, indicating that over 200,000 volumes of water could be treated with one volume of resin. The cost of the resin is approximately $0.24 per 1000 gal of water.

I. INTRODUCTION

The Oak Ridge Y-12 Plant, a Department of Energy site, has large water streams with low concentrations of mercury. The Upper East Fork Poplar Creek (UEFPC) Characterization Area at the Oak Ridge Y-12 Plant is managed by environmental restoration personnel and is regulated by National Pollutant Discharge Elimination System permits from the state of Tennessee. The flow, which is 1700 gal/min at the upper portion of the creek, contains low levels of mercury in the range of 1000 ng/L. The desired treatment goal is 12 ng/L. The UEFPC receives water from various sources, some of which have already undergone limited mercury treatment. Some of the identified sources have flows in the range of 1 to 10 gal/min, with mercury concentrations of 2–40 μg/L.

The following results are from isotherm experiments conducted with UEFPC water at a location known as Outfall 200. The purpose of this study was to screen sorbents for treatment applicability to this stream.

II. METHODS

A. Mercury Sorbents

Many sorbents have been developed for the removal of mercury and heavy metals from waters; however, most of the majority of data published to date do not address the removal of mercury to the target levels represented in this project. The application where these sorbents are targeted for use is in the removal of mercury from microgram-per-liter levels to low nanogram-per-liter levels. Sorbents with thiouronium, thiol, amine, sulfur, and proprietary functional groups were selected for these studies. Several of these sorbents have previously been used to remove mercury from groundwater.

Ionac SR-3 (Sybron Chemicals, Inc.) is a commercial macroporous polystyrene/divinylbenzene resin with (iso)thiouronium functional groups. This sorbent has been found by the manufacturer to bind ionic mercury(II), methyl mercury, and elemental mercury and cannot be regenerated. It performs best at pH values between 0 and 6. At higher pH levels, the thiouronium group is converted to a thiol group. The cost of SR-3 is approximately $12/L. A similar resin is Purolite S-920 prepared by the Purolite Company ($24/L).

Ionac SR-4 (Sybron Chemicals, Inc.), a macroporous, weakly acidic polystyrene/divinylbenzene cation resin with thiol functional groups, is commercially available at a cost of about $14/L. It can be used at pH values ranging from 1 to 14. The recommended flow rate is 0.3 bed volumes (BV)/min. Other materials with similar functionality are Duolite GT-73, by Rohm and Haas ($35/L), and SAMMS (Self-Assembled Mercaptan on Mesoporous Silica), a new inorganic thiol resin developed by Pacific Northwest National Laboratory (PNNL), that is not yet commercially available. The predicted cost of SAMMS is $50/L. PNNL has presented data indicating that elemental and organic mercury may be adsorbed by SAMMS. In general, the thiol resins can sorb only mercury(II) ions.

Keyle:X (SolmetexX) is polystyrene/divinylbenzene resin coated with a proprietary polymer with sulfur-based functional groups. Keyle:X is a mercury-specific resin that
operates at high flow rates (0.2 to 2 BV/min). The manufacturer recommends that the water be pretreated with chlorine to 1–2 mg/L to ensure that the mercury is in the ionic state. The cost is $126/L.

The Forager Sponge (Dynaphore, Inc.) is an open-cell cellulose sponge incorporating an amine-containing polymer that has selectivity for both cationic and anionic species of mercury and other heavy metals. It has the advantage of being a very porous compactible sponge; thus, column capacity can easily be adjusted by altering the packing density. The sponge can be pretreated with acid or base to change functionality (anionic versus cationic). The cost is $5/L.

Mersorb LW, Mersorb 3, and Mersorb 1.5 mm (Nucon International, Inc.) are commercial carbons impregnated with sulfur. The only difference between the three is particle size. Since the sorption is dependent on precipitation of the sulfide, competing metal ions are those that form strong sulfide bonds. The cost is $5/L.

B. Experimental Procedure

The batch sorption experiment was conducted with water collected from East Fork Poplar Creek at Outfall 200 at the Y-12 Plant. The water was filtered through a nominal 1-μm filter. The pH of the water was approximately pH 8 and cations present in the water were aluminum (0.05 mg/L), barium (0.06 mg/L), boron (0.4 mg/L), calcium (50 mg/L), iron (0.2 mg/L), sodium (9 mg/L), magnesium (10 mg/L), manganese (0.1 mg/L), potassium (2 mg/L), and zinc (0.07 mg/L). The mercury concentration was approximately 750 ng/L. Sulfate and nitrate made up the corresponding anions.

The batch isotherm samples were placed in 250-mL I-Chem bottles with Teflon-lined closures. Sorbent masses were approximately 0.225, 0.45, 2.25, and 4.5 g; the solution volume was roughly 150 mL. The bottles were mixed on a Labquake® shaker for 24 h at room temperature (22 to 24°C). The aqueous phase was separated by using a Whatman Autovial syringe filter with a 0.45-μm-pore membrane filter and transferred to a clean 125-mL I-Chem bottle prior to refrigeration, shipment, and analyses. The sample set included several quality control samples:

1. a process blank containing nanopure water,
2. a stream sample that was not processed but was immediately refrigerated after collection (b),
3. a stream sample that had been fully processed but without sorbent (pc), and
4. a duplicate of a sorbent-treated stream sample.

No preservative was added to any of the samples before shipment. Frontier Geosciences, Inc., (Seattle, WA) carried out the mercury analyses. The samples were oxidized with 1 vol % 0.2 N BrCl and analyzed by SnCl2 reduction, dual gold amalgamation, and cold vapor atomic fluorescence detection for total mercury.

Six samples in the batch sorption experiment were spiked with mercuric nitrate to augment the total mercury content; two water samples were not spiked with mercury. The sorbents were used as received from the manufacturers, except in the case of Keylex, which was washed in nanopure water according to directions.

The sorption capacity was calculated using three different methods to account for various losses during the treatment procedure. In the first estimate of  of sorption capacity divided by equilibrium concentration), the mercury concentration in the process blank was subtracted from each of the reported analytical results to calculate a net final mercury concentration in each of the treated samples. The initial mercury concentration was assumed to be the net mercury content of the unprocessed, refrigerated sample (b), plus any spike added to the sample. The for each treated sample (i) was then calculated as follows:

\[ K_d = \frac{[Hg]_{i}^{net} + [Hg]_{i}^{spike} - [Hg]_{i}^{net}_0}{[Hg]_{i}^{net}_0} \times V_i. \]

This calculation assumes that all of the mercury removed from the water was retained on the sorbent. In the second estimate of  was to assume that primary to sorption on equipment “walls.” A sorption ratio for the walls was calculated by assuming that the initial net [Hg] was represented by the untreated stream sample (b) that was immediately refrigerated. The final [Hg] was assumed to be that of the processed sample (plus spike) that did not contain sorbent (pc):

\[ K_d^{wall} = \frac{[Hg]_{b}^{net} + [Hg]_{pc}^{spike} - [Hg]_{pc}^{net}}{[Hg]_{pc}^{net}} \times V_{pc}. \]

The  for each sample (i) was then calculated as follows:

\[ K_d = \frac{[Hg]_{b}^{net} + [Hg]_{i}^{spike} - [Hg]_{i}^{net}_0}{[Hg]_{i}^{net}_0} \times V_i - K_d^{wall} \times [Hg]_{i}^{net}_0 \times W_i. \]

The third method for estimating  was to assume that each sample lost a fixed fraction of mercury as a result of volatilization and sorption onto equipment walls. The fractional loss was calculated based on the ratio of mercury concentration in the processed sample without sorbent (pc) to that of the refrigerated sample (b) plus the amount of...
mercury initially added to the processed sample. The initial mercury concentration was then multiplied by the correction factor, \( cf \), to determine \( K_d \):

\[
 cf = \frac{[Hg]_{pc}^{net}}{[Hg]_{pc}^{net} + [Hg]_{pc}^{spike}}, \quad \text{and} \quad K_d = \frac{\left( cf \times ([Hg]_{b}^{net} + [Hg]_{spike}^{net}) - [Hg]_{spike}^{net}\right) \times V_i}{[Hg]_{i}^{net} \times W_i}.
\]

III. RESULTS

All process blanks (nanopure water) indicated a mercury content of <2 ng/L. The small concentrations observed could be present due to an existing contamination in the water or could come from the equipment used in the experiments. The three methods for calculating \( K_d \) gave almost identical results regardless of the correction method used. The isotherm plots are shown in Figures 1 through 5, in which the sorbent loading (calculated using the second correction method) has been plotted as a function of the equilibrium concentration.

Several results are evident. The data from the experiment conducted with thiuronium-based resin show significant scatter (Figure 1). One possible explanation may be that the sorbent partially broke down in the neutral water, producing a thiol-based resin. It is also evident from the results that Ionac SR-4, Keyle:X, and Mersorb were able to remove mercury in the unspiked creek water to values below 12 ng/L (target goal) at the sorbent-solution volume ratios tested.

Some of the data in the low-concentration region appear scattered (see Figures 2 and 5). Without additional experiments, it is difficult to determine which of the points are suspicious. The fact that the points do not seem to fall on the straight line may indicate that the form of the mercury in solution does not match that of the spiked solution. It is possible that a fraction of the mercury is present in the elemental form (Hg\(^0\)), which may be converted to Hg\(^+\) in the presence of a larger amount of Hg\(^+\), which is found in the spiking solution. Ionic mercury is predominantly the sorptive species. This would explain why there was more mercury in solution at equilibrium in some unspiked experiments (open symbols) than in some spiked experiments (closed symbols).
Table 1 summarizes results for the treatment of a 1000-ng/L stream using $K_d$ calculated by the second correction method. As noted, the thiol-based resin (Ionac SR-4) performed much better than the others. The results indicate that 16,700 L of Outfall 200 water can be treated for $1 (resin cost). This corresponds to a cost of approximately $0.24/1000 gal water. The flow at Outfall 200 is approximately 2.5 million gallons per day; thus, the average daily cost for the resin would be about $600.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>$K_d$, dry basis (L/kg)</th>
<th>$K_d$, bed basis (L/L_w)</th>
<th>$K_d$, cost basis (L/$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionac SR-3</td>
<td>50,000</td>
<td>26,700</td>
<td>2,200</td>
</tr>
<tr>
<td>Ionac SR-4</td>
<td>500,000$^d$</td>
<td>235,000</td>
<td>16,700</td>
</tr>
<tr>
<td>KeylEx</td>
<td>250,000</td>
<td>67,700</td>
<td>540</td>
</tr>
<tr>
<td>Forager Sponge</td>
<td>3,000</td>
<td>270$^b$</td>
<td>54$^e$</td>
</tr>
<tr>
<td>Mersorb 1.5 mm</td>
<td>70,000</td>
<td>39,500</td>
<td>7,900</td>
</tr>
</tbody>
</table>

$^a$Calculated as sorbent capacity (ng mercury/kg dry sorbent) + [1000 (ng mercury/L water)].

$^b$Calculated as $[K_d$ (dry basis)] × (1 − moisture content) × [bulk density (kg/L)].

$^c$Calculated as $[K_d$ (bed basis)] × [cost ($/L_w$)].

$^d$Extrapolated value.

$^e$These values can be increased by packing the Forager Sponge more tightly.

**IV. CONCLUSIONS**

Mercury was successfully removed from surface (creek) water and mercuric-nitrate-spiked surface water via adsorption onto several different resins, to levels below the target goal of 12 ng/L. The results showed that a thiol-based resin (Ionac SR-4) gave the best performance, indicating that over 200,000 volumes of water could be treated with one volume of resin. The cost of the resin is approximately $0.24 per 1000 gal of water.

**NOMENCLATURE**

- $cf$ correction factor
- $[Hg]$ mercury concentration (ng/L)
- $K_d$ sorption distribution coefficient (L/kg)
- $V$ volume of liquid (L)
- $W$ weight of sorbent (kg)

**ACKNOWLEDGEMENTS**

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**REFERENCES**
