Removal of Soluble Mercury from Water by Rubber

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Rapid development of energy sources is bringing an increase in industrial processes involved with mercury. The vapor and effluent waste of such industry usually ends up, directly or indirectly, in nearby large bodies of water resulting in the ruin of adjacent fishing grounds (HUGUNIN and BRADLEY, 1975). As a consequence, effective methods need to be found for the removal of trace levels of organic and inorganic mercury compounds present in industrial waste water. Mercury contaminated sediment could be sealed with a covering layer (BONGERS and KHATTAK 1972, WIDMAN and EPSTEIN 1972), or mercury removed through chemical adsorption by various agents (SUGGS et al. 1972). The most effective mercury adsorbing agents are those containing high amounts of sulfur (LEE and RICHARDSON 1973, TRATNYEK 1972) but this process is seriously affected by competition from the sediment which also contains sulfur.

The most practical approach to the control of mercury pollution would seem to be one of prevention; purifying the effluent waste prior to its discharge. MAAG and HECKER (1972) developed a chemical displacement technique using aluminum foil for effluent purification and recovery of metallic mercury. Chelating polymers of various types are also effective in mercury removal from solution (LAW 1971, MICHELSON et al. 1975). NETZER et al. (1974) and NOYES et al. (1975) reported that ground rubber could be used to remove organic and inorganic forms of mercury from water. This report describes the results of a study using columns of ground rubber or active carbon for removal of inorganic mercury from water.

Materials and Methods

Counting Systems. A radiotracer technique was used because of ease and accuracy with which very small amounts of mercury could be detected. In this study, radioactive mercury nitrate, $^{203}Hg(NO_3)_2$ in 0.1 N HNO_3, obtained from New England Nuclear Co. (Boston, Mass.) was used. This stock solution had a specific activity of 17.8 mCi/mg and a total solids content of 5.6 mg Hg^{2+}/

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ml. A 4.9 ml volume of deionized distilled water (DDW) was added to the stock solution. An aliquot (5 µl), when added to the vial containing 10 ml DDW, yielded a tracer solution of 0.056 µg Hg^{2+}/ml (carrier free - CF). Other tracer solutions were supplemented with Hg^{2+} carrier, as $HgCl_2$, to yield 50 or 500 µg Hg^{2+}/ml. An aliquot of each solution was then placed in a plastic scintillation vial containing 10 ml of New England Aquasol liquid scintillation fluor and counted in a Beckman LS-100 C liquid scintillation spectrometer to determine initial activity. Most samples were counted to ±1% erro but those with less than 500 CPM (following cycling through the column) were counted to not less than 5% error. All data were corrected for background and half-life.

Preparation of the column. Small columns containing measured quantities of either ground rubber (GR) or active carbon (AC) were constructed. The GR was prepared as previously described (NOYES *et al*. 1975), and the particles ranged in size from 10 to 200 µ. Desired amounts were placed in a test tube containing 10-15 ml DDW and made thoroughly wet by heating twice at 121 C for 15-30 min. AC was prepared by grinding activated filter carbon (Harts Mountain Corp., N.J.) in a mortar and pestle followed by sieving to obtain particles between 0.42 and 0.84 mm diameter for use in the column. The chromatograph columns were made from 10 ml (80 x 14 mm) disposable plastic syringes (Becton, Dickinson & Co., N.J.) plugged with a small piece of glass wool (Pyrex). The desired adsorbent (AC, 0.5 g; GR, 0.5 or 1.0 g) was then added to the column and washed several times with DDW. Columns containing the glass wool plug and no added adsorbent served as controls.

Recycling Procedure. Ten milliliters of each ^{203}Hg^{2+}-solution, CF or with carrier (50 or 500 µg Hg^{2+} ml), was delivered to the top of the column, allowed to flow freely, and the entire effluent collected in a 20 ml polyethylene vial. The effluent was recirculated through the column for 10 cycles and the elution of each cycle required approximately 10 sec regardless of the type of adsorbent. Aliquots (5 µl) were removed from the effluent after each cycle and counted to ascertain the decrease in activity of the ^{203}Hg^{2+}-solutions due to adsorption by the test adsorbent. The results, representing an average of six experiments, were expressed after each cycle as percent cumulative decrease (CD) in radioactivity of the solution compared to the initial activity.

Results

Removal of $^{203}Hg^{2+}$ from solution.

Control column. Data (Table 1) demonstrated a reduction in counts after each cycle with the CF solution showing a higher rate of adsorption. Therefore, unless stated otherwise, all data were corrected for adsorption by the control system in order to ascertain the true effect of each adsorbent on the removal of ionic mercury.

TABLE 1.

Cumulative decrease (%) in $^{203}Hg^{2+}$ activities from solutions cycled through the control column.

Cycle No.	Mercury in solutions (µg Hg^{2+}/ml)		
	0.056[a]	50	500
1	20.30 ±1.98[b]	4.25 ±2.76	3.20 ±0.42
2	22.10 ±0.71	7.90 ±2.12	1.50 ±2.55
3	25.80 ±4.95	7.90 ±2.83	2.50 ±2.97
5	27.00 ±2.26	5.20 ±1.98	3.45 ±1.48
10	38.95 ±0.21	9.40 ±3.11	1.10 ±4.53

[a] Carrier-free $^{203}Hg^{2+}$ solution

[b] Standard deviation

Active carbon column. Figure 1 shows the data obtained when 0.5 g AC was used as an adsorbent and indicates that the $^{203}Hg^{2+}$ was removed immediately from the CF solution. Approximately 25% of the initial activity was adsorbed following the first cycle. A maximal CD of 35.3 ± 2.1% occurred after the fifth cycle, with very little change thereafter. In the presence of 500 µg Hg^{2+} carrier/ml solution, the CD was slight but steady and reached 18.7 ± 2.8% after the 10th cycle. This CD was about 2/3 of that noted after the 10th cycle for the CF solution.

Ground rubber column. Figure 1 also depicts the results obtained using GR as adsorbent. When the column

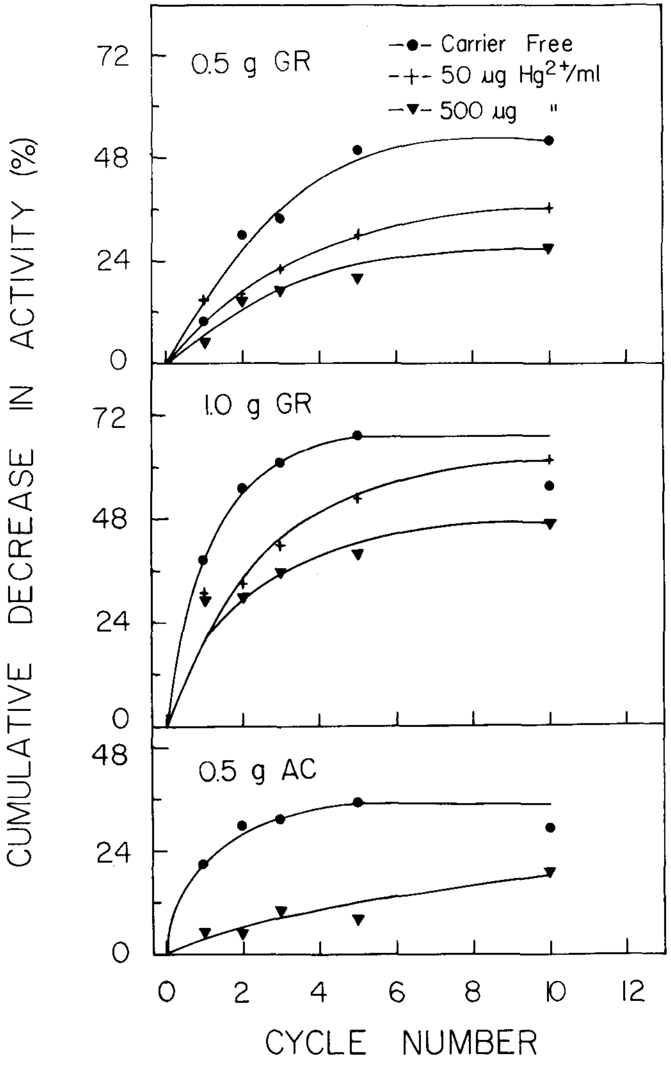

Figure 1. Effect of ground rubber (GR) and active carbon (AC) on the removal of $^{203}Hg^{2+}$ from different solutions. Results, representing an average of six experiments, are reported as % cumulative decrease (CD) in radioactivity as compared to the initial. Experimental conditions are described in Material and Methods and all values have been corrected for adsorption by the control system.

contained 0.5 g GR the rate of adsorption of $^{203}Hg^{2+}$ was correlated with Hg^{2+}-carrier level and cycle number. Using CF solution, the CD after the fifth cycle was 49.7 ± 2.9% with only a slight adsorption thereafter. When the $^{203}Hg^{2+}$-solution was supplemented with 50 and 500 µg Hg^{2+} carrier/ml the CD were 36.6 ± 0.2% and 27.2 ± 4.1%, respectively, after the 10th cycle. Similar effects, but higher in magnitude, were noted when the amount of GR adosrbent in the column was increased to 1.0 g and the CD at the end of the 10th cycle were: 55.3 ± 2.5% (CF), 61.3 ± 1.4% and 47.2 ± 0.4% (50 and 500 µg Hg^{2+} carrier/ml, respectively). Comparative analysis of the data for the two levels of GR at the end of the 10th cycle showed that the rate of removal of $^{203}Hg^{2+}$ from solution increased as the GR concentration increased. For example, a slight difference in adsorption (CD of 51.40 ± 2.40 for the 0.5 GR column as compared to 55.30 for the 1.0 g GR) was noted when CF solution was used. In the presence of 50 and 500 µg Hg^{2+} carrier/ml solutions the difference in the rate of removal of $^{203}Hg^{2+}$ was significantly greater for columns containing 1.0 g GR. A three way analysis of variance of the CD in activities was conducted relating GR levels (no GR, 0.5 and 1.0 g), $^{203}Hg^{2+}$ concentration (CF, 50 and 500 µg Hg^{2+} carrier/ml), and cycle number. The results indicated that only the adsorbent and Hg^{2+} concentration significantly affected the removal of $^{203}Hg^{2+}$ ($P<0.05$) and that there were no significant interactions among the aforementioned factors.

Assuming that no preference for adsorption occurred between $^{203}Hg^{2+}$ and Hg^{2+} and that the CD of the tracer in solutions cycled through the column also reflected the removal of the Hg^{2+}, then the actual amount of $^{203}Hg^{2+}$ and Hg^{2+} adsorbed could be calculated using the following equation:

$$\text{Specific Adsorption } (\mu g\ Hg^{2+}/g\ GR) = \frac{CD \times Hg^{2+} conc. \times V}{\text{adsorbent wt.}}$$

In this equation, CD represents the total radioactivity adsorbed (cumulative decrease) expressed as a fraction of initial activity; Hg^{2+} concentration denotes mercury level (µg/ml); V is the volume cycled (10 ml); and adsorbent weight represents the amount used in the column (g). The specific adsorptions of the three different mercury solutions in either GR column were plotted as a function of cycle number (Fig. 2) and the data confirmed the results of the statistical analysis. As Hg^{2+} concentration increased more mercury was adsorbed, with each

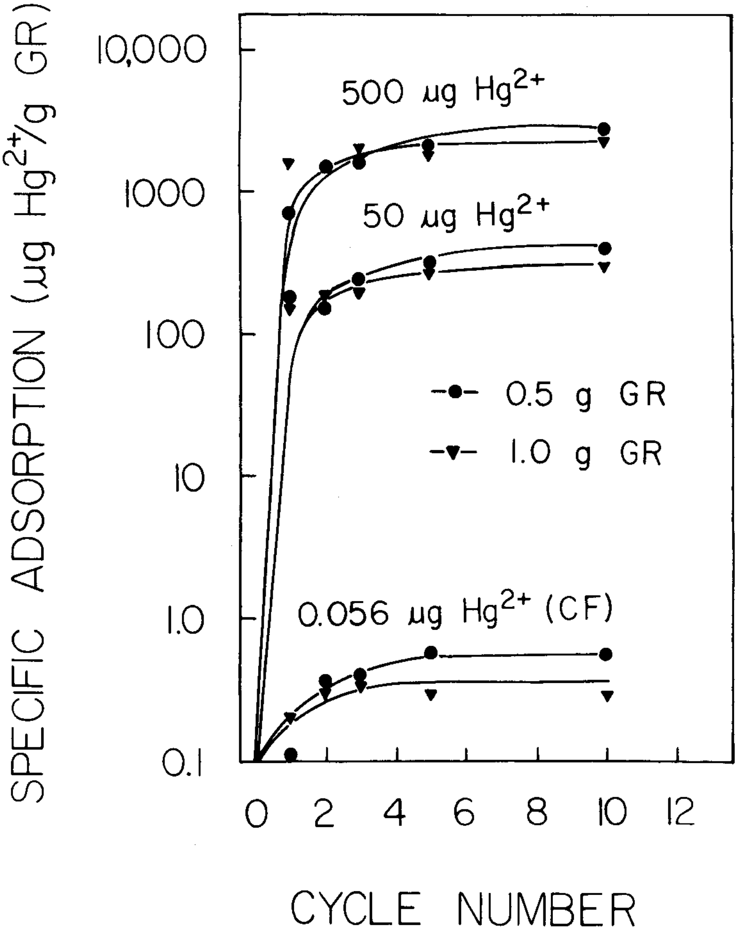

Figure 2. The specific adsorption (µg Hg^{2+}/g GR) as a function of number of cycles through 0.5 or 1.0 g GR columns for solutions containing different levels of Hg^{2+}.

solution reaching equilibrium about the 3-5th cycle. A logarithmic relationship evidently existed between specific activities and Hg^{2+} concentration in the solution cycled. Therefore, a regression analysis of log specific activities on log Hg^{2+} concentration was conducted at the end of 10 cycles for each GR level and the following equations prepared:

Log specific activity after 10 cycles in 0.5 g GR column.

$$1\ A_{0.5g} = 0.938 + (0.943 \times \log Hg^{2+}\ \text{concentration})$$

Log specific activity after 10 cycles in 1.0 g GR column.

$$1\ A_{1.0g} = 0.744 + (0.990 \times \log Hg^{2+}\ \text{concentration})$$

The correlation coefficients for both GR levels were greater than 0.99 and the regression effect was significant at the $P<0.0005$ level.

Discussion

The decrease in $^{203}Hg^{2+}$ activity from solutions, particularly the CF, cycled through the control column is due to chemisorption by walls of the column and vial, as well as by the fiberglass plug. This data is supported by BENEŠ and RAJMAN (1969), NEWTON and ELLIS (1974) and NOYES et al. (1975). However, volatilization, via disproportionation, may occur in solutions of Hg^{2+} ion if small amounts of reducing agents are present in reagents or demineralized water (TORIBARA et al. 1970; GILMOUR and MILLER 1973). In the present investigation the entire process of recycling the Hg^{2+} solution to the 10th cycle was probably too short (~ 2 min) to allow for any appreciable volatilization.

The basis for adsorption of Hg^{2+} by GR may lie in its composition. Native rubber consists of long chains of polymerized isoprene subunits. The process of vulcanization, which involves heating the rubber in the presence of sulfur, introduces crosslinkages between the chains through the sulfur groups. This results in the presence of some free sulfur and combined sulfur as well as sulfides, sulfites, and sulfates. These sulfur compounds could bind with Hg^{2+} weakly or strongly and may form several coordinated structures. Other materials used in formulating rubber which may be important in the adsorption of mercury are the fillers and reinforcing agents. Carbon black is probably the most significant compound of this type as its behavior appears to be much like that of active carbon (Blow 1971). Considering the affinity of mercury for sulfur as well as active carbon, it is likely that a combination of these factors accounts for the adsorption of mercury by rubber.

The equations relating the logarithmic relationship between specific activity and Hg^{2+} concentration could provide a basis for predicting the actual amount of Hg^{2+} removed from solutions of known Hg^{2+} concentration. However, more efficient removal might be realized if effluent containing Hg^{2+} was concentrated prior to cycling it through GR columns. Because of the equilibrium nature of Hg^{2+} removal by GR, the process could be used to reduce levels to that where more expensive, but thorough, methods would be practical. Beckman et al. (1974) suggested converting scrap rubber into a cation exchange material, after noting that waste rubber particles used as a partial carbon source for microbial fermentation had significant cation exchange abilities resulting from a layer of organic molecules coating the rubber particle surfaces. A process whereby rubber is used first as a substrate for protein production and then as an agent for mercury decontamination of polluted effluent would maximize the potential reuse of a waste material.

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