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Removal of Mercury and Methylmercury from Waste Waters by Sorption

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The toxicity of mercury and its compounds is well known and their presence in natural waters has been recognised as an environmental hazard in many countries. In aquatic systems, the bivalent inorganic mercury is the predominant species and the different compounds of mercury including metallic mercury are converted initially to this form. Subsequently, biological and non-biological processes convert this form into methyl and dimethyl mercury (JENSEN and JERNELOV 1969, WOOD et al. 1968, AKAGI et al. 1977). The possibility of removing heavy metals from effluent and natural waters has, therefore, some importance in connection with toxic effects on man.

Low cost organic materials were shown (HENDERSON et al. 1977) to sorb heavy metal ions from aqueous solutions. The solutions used in those studies were prepared from distilled water and furthermore high concentrations of heavy metal ions were used. Specifically, mercury solutions were prepared with distilled water at concentration of 112 ppm. In order to simulate conditions comparable to municipal waste waters, levels of perhaps 1,2,5 and 10 ppm would be more appropriate (ABBOTT 1971).

Surface waters contain dissolved organic matter which bind heavy metal ions (RAMAMOORTHY and KUSHNER 1975a). The heavy metal binding capacity of the Ottawa River water for example (Hg^{2+} (RAMAMOORTHY and KUSHNER 1975b) was found to be 21 µM of Hg^{2+} ion. This value has been reaffirmed from recent analysis (LAUBE et al. 1978). The present paper reports the results of studies of (i) sorption at environmental levels of mercury which are 1-2 orders of magnitude lower than the previous studies, (ii) the effect of heavy metal binding components present in the river water in contrast to distilled water in the heavy metal removal processes, and (iii) removal of methyl mercury from aqueous solutions by low cost organic materials.

EXPERIMENTAL

Ground rubber and soft wood saw dust were used as sorbents in this study. These materials are available as solid wastes from a few industrial operations and cost approximately $ 3-5/ton. Four size fractions of 0.075, 0.15, 0.7 and 1 mm of each material

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were used in the mercury removal studies. Experiments were conducted on both inorganic and methyl mercury in river water and distilled water solutions. Initial concentrations of 1,2,5 and 10 ppm of both inorganic and methyl mercury were used in all sorption experiments, in order to simulate natural conditions. Mercury and methyl mercury analysis were conducted by a tracer technique using radioactive ^{203}Hg (half life = 47 days; γ ray energy = 0.270 million electron volts (MeV)), using a deep well counter. Mercuric nitrate was used as the source of inorganic mercury both in stable form and radioactive form. Methyl mercuric Chloride was used in both stable and radioactive forms.

Deionised water was used in the studies. The Ottawa River water used in the study had the following physico-chemical characteristics: Eh, +345- + 430 mV; pH, 7.80 - 7.70; pCl, 3.80 - 3.60; Conductivity, 21 - 22 µmhos; complexing capacity, 21 µM of Hg^{2+}. One gram of the sorbent was added to 100 ml of the medium containing inorganic mercury or methyl mercury and was left gently agitating on a platform shaker. The samples were withdrawn at 1 h and 24 h and analyzed for mercury content both in water and in sorbent phases.

RESULTS AND DISCUSSION

The results are given in Figures 1-2, as the amount of mercury left non-sorbed in the water phase in presence of the sorbent.

Figure 1 presents the data of sorption of inorganic and methyl mercury by ground rubber (size fraction 0.15mm) from solutions of different initial concentrations of 1, 2, 5, 10 ppm. The data show that for the same initial concentration, more methyl mercury remains in the solution phase unsorbed by ground rubber, as compared to the inorganic mercury. The amounts of ground rubber used in both the experiments were the same and other experimental conditions were similar. For example, for an initial concentration of 10 ppm about eight times more methyl mercury resides in the water phase (Figure 1) compared to inorganic mercury. The fraction of the initial inorganic mercury sorbed from both river water and deionized water is constant over the range 2 - 10 ppm and is around 0.94 and 0.95 respectively. A small amount of inorganic mercury 0.09 ppm is in the bound form in the river water which is not removed by ground rubber in the concentration range studied. This is shown by the difference between the solid and broken lines for inorganic mercury. (Figure 1). The absence of such a drop in the case of methyl mercury suggests that it does not bind strongly to the dissolved organics in the water column.

The saw dust reacts with the two mercuric compounds in just the opposite manner. For comparable concentrations, saw dust sorbs more of methyl mercury and less of inorganic mercury (Figure 2). The sorption of inorganic mercury by saw dust is the same for river water and deionized water suggesting that the organic content of the saw dust might be acting in addition to sur-

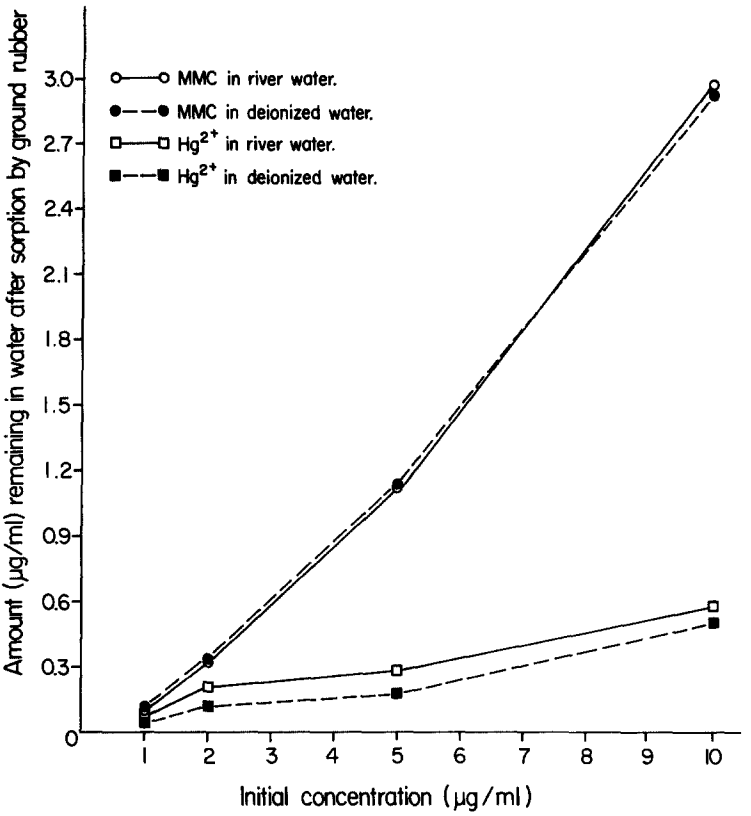

Fig. 1. Sorption of mercury and methyl mercury by ground rubber from deionized and river water.

face action in removing the residual mercury bound to the organics in the river water. This does not seem to work in the case of methyl mercury (Figure 2). This might be due to (i) less surface affinity which is expected on the basis of reduced charge on the molecule CH_3Hg^+ as compared to Hg^{2+} and (ii) the organic sites on the saw dust may not be simple coordination sites to bind methyl mercury but may very well chelate the inorganic mercury due to the difference in the coordination chemistries of the two mercuric compounds as explained later in this paper.

The data on percent removal of the two mercuric compounds by ground rubber and saw dust in both river water and deionized water are given in Table 1.

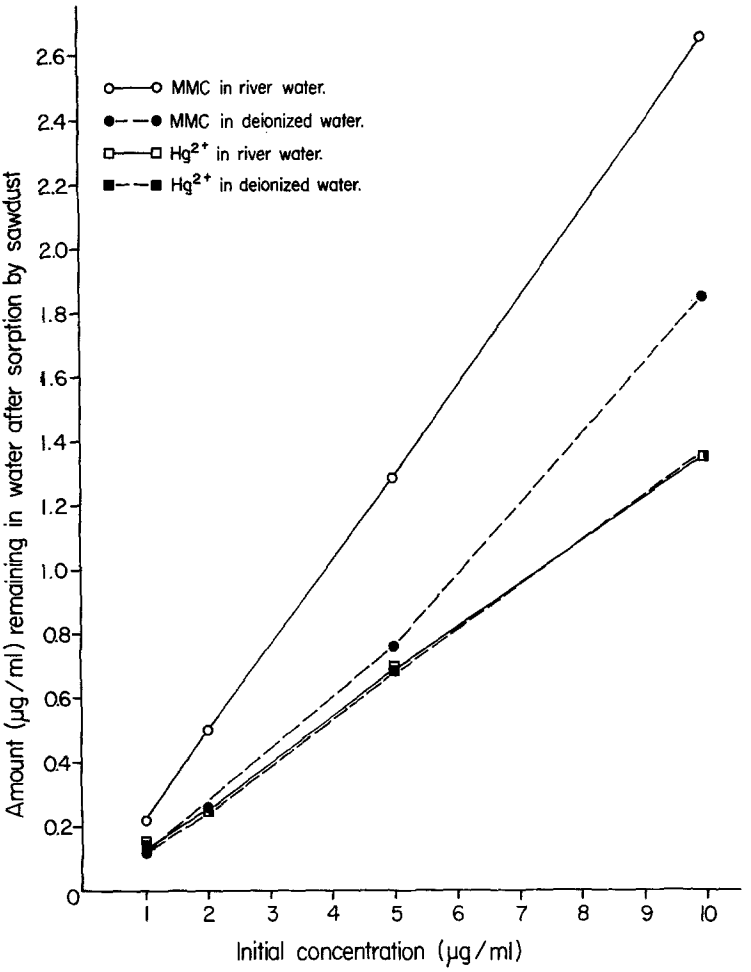

Fig. 2. Sorption of mercury and methyl mercury by saw dust from deionized and river water.

From the Table it is clear that the effect of the dissolved organics in the river water in the mercury removal processes is minimal to nil in the range of 1 - 10 ppm. This was surprising since the Ottawa River water has a heavy metal binding capacity of 21 µM of Hg^{2+} capable of holding mercury in the bound form with a conditional constant of 1.25×10^6 (RAMAMOORTHY and KUSHNER 1975). Obviously, the bonding constants of the mercuric compounds to the surface sites of ground rubber as well as saw dust must be higher than 1.25×10^6 , with the exception of methyl mercury curves in Figure 2. The amount of methyl mercury left unsorbed

TABLE 1

PERCENT REMOVAL OF ADDED MERCURY

Compound	Ground Rubber		Saw Dust	
	River water	Deionized water	River water	Deionized water
Inorganic mercury	94	95	87	87
Methyl mercury	70	70	74	82

in the river water is reasonably close to the value obtained with the corresponding one with ground rubber, but the removal from the deionized water is 8% higher than the river water. The same difference was observed in mercury removal experiments using different size fractions of sorbents at a constant concentration of 1 ppm.

The percent sorbed remained constant for the various size fractions of the sorbents tested in this study.

Mercury being a soft acid (AHRLAND 1966) forms strong covalent complexes with soft bases such as N, S, Se etc.. These donor atoms could be part of micro solutes dissolved in natural waters, or biota or part of the organic matter of the sediment. In addition to complexing with natural and/or synthetic ligands, mercury can also interact with surfaces of organic and inorganic origin through physico-chemical sorption processes. These processes have been successfully employed in the reclamation and heavy metal scavanging operations of the polluted waters. Methyl mercury forms complexes with a variety of orgnaic and inorganic ligands with a coordination number of one. In fact, this simple straight forward coordination of methyl mercury makes it a highly selective reagent for sulphydryl groups and as a chemical probe for unpaired bases in DNA. By comparison, the residual Lewis acidity in RHgX is small relative to HgX_2. The formation constants of methyl mercury with several organic ligands (RABENSTEIN 1978) reported in literature vary widely in range and generally smaller than those corresponding to Hg^{2+}. Pearson (1973) attributed this decrease to the soft base CH_3^- ligand on Hg in CH_3Hg^+ decreasing the affinity of Hg towards other ligands.

The present study revealed that ground rubber and saw dust are efficient in removing mercury and methyl mercury from water at environmentally contaminated levels expected in several point source discharges. The organics present in the river water do

not affect the mercury removal efficiency of these sorbents. The slightly higher percentage removal of mercury by ground rubber could be offset by the abundance and ease of availability of saw dust at several locations in Canada. Both of them could be disposed on land by common procedures, but the saw dust might degrade faster than ground rubber releasing the mercury to the soil organic matter. Whereas, the ground rubber might resist degradation either microbially or otherwise and thus maintaining its structural integrity. Still, some mercury could be lost from it through leaching by soil organic matter or ion exchange with other soil cations. On the basis of the results obtained under the experimental conditions mentioned in this study, about half a ton of saw dust or ground rubber might be sufficient to "clean up" 1000 gallons of water, removing most of the mercury.

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