# Competitive Adsorption of Metal Ions From Solutions by Low-Cost Organic Materials

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#### Introduction

Land application of wastewater and sludge containing heavy metal ions can be a long term hazard (ANONYMOUS 1973; BERROW and WEBBER 1972; DAVIES 1972; WEBBER 1972). It is not uncommon for wastewater or sludge to contain 10 to 25 times the heavy metals content appropriate for land application (ABBOTT 1971). Accumulation of heavy metals in the soil can result in toxicity to plants grown on the land or to animals that consume these plants.

Previous work has shown that peanut hulls, raw southern pine bark, and composted bark will remove significant amounts of various heavy metals ions from solution (HENDERSON, LIGHTSEY, and POONAWALA 1976). The present investigation concerns the ability of softwood sawdust, corncobs, and finely-ground scrap rubber to remove heavy metals such as Cd, Zn, Cu, Hg, and Ni from wastewater.

### Materials and Methods

#### Materials

Softwood sawdust, corncobs, and finely-ground scrap rubber were studied as to their adsorbent properties. The availability, approximate costs, and physical properties of the solid wastes are given in Table 1.

The three solid wastes shown in Table 1 were tested as received. To determine the effect of solid waste surface area on adsorption, two size fractions of softwood sawdust and finely-ground scrap rubber were also tested: 177-210 microns (80 mesh) and 100-105 microns (150 mesh). The average particle size of the wastes were calculated from the sieve analysis data (MCCABE and SMITH 1967).

TABLE 1

Availability, Cost, and Physical Properties of the Solid Wastes Used in this Investigation.

Organic Wastes	Production In U.S. (tons/yr.)	Approx. Cost (\$/ton)	Percent Water +	Average Particle Size *	
Softwood Sawdust	720,000	3	50	1428	
Corncobs	500,000	8	12	2517	
Ground Scrap Rubber	70,000	5	0	909	

+ The samples were dried for 2 hours at  $110^{\circ}$ C.

\* Volume surface mean diameter (MCCABE and SMITH 1967).

#### Reagents

Solutions of heavy metal ions at the concentrations expected in municipal wastewater (ABBOTT 1971) were made by dissolving the reagent grade metal salts  ${\rm HgCl_2},~{\rm CuCl_2}\cdot {\rm 2H_2O},~{\rm Ni(NO_3)_2}\cdot {\rm H_2O},~{\rm CdCl_2}\cdot 2.5{\rm H_2O},~{\rm and}~{\rm ZnSO_4}\cdot 7{\rm H_2O}$  in distilled water.

#### Method

Each of the solid wastes investigated was tested as described in an earlier report (HENDERSON, LIGHTSEY, and POONAWALA 1976).

## Discussion of Results

As Table 2 shows, wood fines were not very effective in adsorption of heavy metals. Only Cu and Ni were retained by the fines in appreciable amounts at both high and low metal concentrations. Contrary to expectations, a decrease in the particle size of the wood fines resulted in less adsorption of some metals (Figure 1). This anomalous behavior may be due to the presence of a higher percentage of extraneous material (such as dirt and sand) in the smaller size fractions as compared to the received wood fines.

Corncob fragments, even though relatively large in size, removed a sizeable percentage of Cu and Cd from the low concentration solutions. While corncobs were quite effective when used as received, either composting or mechanical grinding of this material should improve

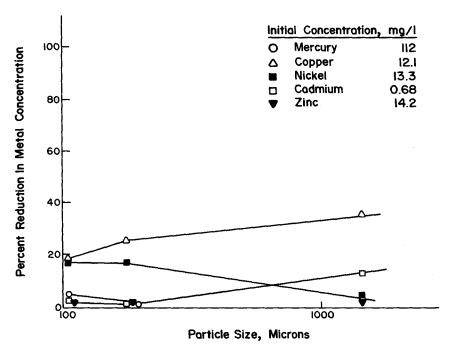


FIGURE 1
Effect of Softwood Sawdust Particle Size on Competitive
Adsorption of Heavy Metals

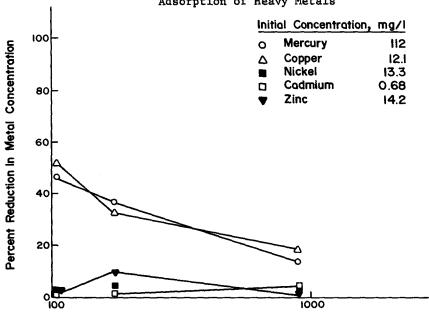


FIGURE 2
Effect of Rubber Particle Size on Competitive Adsorption of Heavy Metals

Particle Size, Microns

		Concentration (mg/1)			Adsorption			
0		Level I		Level II		% Reduction		
Organic Wastes	Heavy Metal	Initial	Final	Initial	Final	Level I	Level II	
Softwood	Hg	112	110			1.8		
Sawdust	Cu	2475	2350	12.1	7.8	5.05	35.54	
(as	Ni	325	325	13.3	12.9	0	3.4	
received)	Cd	65	60	0.68	0.61	7.69	10.29	
	Zn	75 <b>00</b>	7000	142	142	6.66	0	
Softwood	Hg	112	112			0		
Sawdust	Cu	2475	2450	12.1	9.0	1.01	25.62	
(80 Mesh)	Ni	325	325	13.3	11.0	0	17,29	
	Cđ	65	65	0.68	0.68	0	0	
	Zn	7500	7500	142	142	0	0	
Softwood	Hg	112	107			4.46		
Sawdust	Cu	2475	2450	12.1	9.9	1.01	18.18	
(150	Ni	325	325	13.3	11.0	0	17.29	
Mesh)	Cd	65	65	0.68	0.68	0	0	
	Zn	7500	7000	140	140	6.66	1.41	
Corn	Hg	112	109			2.7		
Cobs	Cu	2475	2375	12.1	5.9	4.04	51.24	
(as	Ni	325	300	13.3	13.1	7.69	1.50	
received)	Cd	65	60	0.68	0.53	7.69	22.06	
	Zn	7500	6500	142	134	13.33	5.63	
Rubber	Hg	112	104	~		7.1		
(as	Cu	2475	2375	12.1	9.9	4.04	18.18	
received)	Ní	325	300	13.3	13.1	7.69	1.50	
	Cd	65	60	0.68	0.66	7.69	2.94	
	Zn	7500	6500	142	142	13.33	0	
Ground	Hg	112	69			38.39		
Rubber	Cu	2475	2375	12.1	8.1	4.04	33.06	
(80 mesh)	Ni	325	300	13.3	12.7	7.69	4.51	
	Cd	65	60			7.69	0	
	Zn	7500	6500	142	128	13.33	9.86	
Ground	Hg	112	60	*		46.43		
Rubber	Cu	2475	2350	12.1	5.8	5.05	52,07	
(150	Ni	325	325	13.3	13.3		0	
Mesh)	Cd	65	62.5				1.47	
	Zn	7500	6500	142	142	13.33	0	

the adsorption capacity considerably. The results from the batch adsorption tests involving ground scrap rubber are also given in Table 2. Significant amounts of Hg and Cu were removed from solution by the rubber particles at both solution concentrations, whereas Ni, Cd, and Zn were moderately adsorbed by the rubber at high concentration, and only slightly adsorbed at low concentrations. Apparently, at low concentrations, either the Hg and Cu are more competitive for the adsorption sites, or the concentration gradient for Ni, Cd, and Zn is not sufficient for effective adsorption.

The effect of rubber particle size is very pronounced with Hg and Cu (Figure 2). This is not unexpected since the rubber would have the lowest porosity and the least amount of available internal surface area of all the wastes tested. Although corncobs and rubber are moderately effective in adsorbing Cu and Hg ions, the solid wastes tested during this investigation generally are not as effective as peanut hulls or composted bark in removing all types of heavy metals from solution (HENDERSON, LIGHTSEY, and POONAWALA 1976).

#### Summary

The competitive adsorption of Hg, Cu, Ni, Cd, and Zn by softwood sawdust, corncobs, and ground scrap rubber was investigated. It is concluded that these materials which are abundant, widespread, and low cost, are potentially useful in removing various metal ions from wastewater solutions.

## References

ABBOTT, R.A.: Metals in Municipal Sewage Systems.
Ontario Water Resources Commission 1971.

ANONYMOUS: Water and Sewage Works, July 1973, p.50. BERROW, M.L., and J.W. WEBBER: J. Sci. Food Agric. 23, 93 (1972).

DAVIES, R.: Water and Poll. Contr. 109, 19 (1972). HENDERSON, R.W., G.R. LIGHTSEY, and N.A. POONAWALA: Bull. Environ. Contam. Toxic. (In Press)

McCABE, W.L. and J.C. SMITH: Unit Operations of Chemical Engineering. 2 ed. New York: McGraw-Hill 1967).

WEBBER, J.: Water Poll. Contr., p. 405 (1972).