Reduction of Mercury, Copper, Nickel, Cadmium, and Zinc Levels in Solution by Competitive Adsorption onto Peanut Hulls, and Raw and Aged Bark

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Introduction

Municipal sewage treatment plants involve the use of bacteria to oxidize organic matter in the wastewater. The combining of industrial and municipal waste offers many advantages and is gaining in popularity. However, certain metal ions present in industrial wastes are toxic to bacteria, especially if the metal ions enter the treatment system at a temporary, high level.

Several studies have shown that bacteria are susceptible to the toxic effects of various metal ions (BARTH, et al. 1965; GHOSH and ZUGGER 1973; LAMB and TOLLEFSON 1973; McDERMOTT 1963; MOSHE, et al. 1972). A slug load of only 5 mg/l of Cu was found to reduce the effectiveness of activated sludge by almost 90% (LAMB and TOLLEFSON 1973).

Metal ions can be removed from water by several methods, including ion-exchange, activated carbon, and reverse osmosis (SMITH 1973). However, these methods are generally too expensive to install when only occasional shock loads are expected. Several organic residues have been shown to adsorb metal ions from solution (FRIEDMAN and WAISS 1972). This investigation involves a study of the feasibility of using low-cost, wide-spread organic residues to remove excessive amounts of toxic metal ions from wastewater.

Experimental Program

The adsorbent materials studied included raw and composted southern pine bark, and peanut hulls. Table 1 gives the approximate cost, the amount generated in the U.S. each year, and the physical properties of the materials used in the experiments. All adsorbents were tested as received; in addition, two size fractions of peanut hulls were tested: 177-210 micrometers (80 mesh), and 100-105 micrometers (150 mesh). The average particle sizes of all wastes were calculated from the sieve analysis (McCABE and SMITH 1967).

Adsorbability Tests

In this work the organic wastes were tested in single dosage runs to evaluate their relative ablility to adsorb heavy metals from solution. For these tests a sufficient amount of material as received that would yield

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TABLE 1

Cost, Availability, and Physical Properties (as received) of Organic Wastes used in the Experiments

Organic Wastes	Approximate Cost ($/ton)	U.S. Production (tons/yr)	Moisture Content (%)*	Average Particle Size**
Peanut hulls	12	3.5×10^5	15	3333
Raw pine bark	4	1.9×10^7	20	2381
Composted pine bark	12	not available	49	500

*The samples were dried at 110^o for 2 hours.
**Volume surface mean diameter (McCABE and SMITH 1967).

one gram of waste on a dry basis was placed in a 250-ml flask. To this was added 100 ml of a solution containing reagent grade $HgCl_2$, $CuCl_2 \cdot 2H_2O$, $Ni(NO_3)_2 \cdot H_2O$, $CdCl_2 \cdot 2.5H_2O$, and $ZnSo_4 \cdot 7H_2O$ in distilled water. The solid and solutions were agitated for one hour on a gyratory shaker table. The solids were then removed from the solution by vacuum filtration through No. 2 Whatman filter paper, and the heavy metals concentrations in the filtrate were measured on a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer. The conditions used for each element studied were those specified in the Perkin-Elmer manual, "Analytical Methods for Atomic Absorption Spectrophotometry." A 1 mv Houston Omniscribe recorder was interfaced to the instrument by an Automatic Null Recorder Readout Module. In some cases, samples were diluted to achieve concentrations in the linear region.

All heavy metal solutions were stored in polyethylene bottles to guard against container adsorption (KING et al. 1974). As a further precaution, a control sample of each heavy metal solution was carried through the entire process, including filtration, but without the addition of solid wastes.

Discussion of Results

As Table 2 shows, the organic wastes varied considerably in their ability to adsorb heavy metals from solution. Peanut hulls adsorbed significant amounts of all the heavy metals in competitive adsorption. At high metal concentrations peanut hulls retained 117 mg

TABLE 2

Competitive Adsorption of Heavy Metals by Wastes in One-Hour Batch Tests

Organic Waste	Heavy Metal	Concentration (mg/l) Level I Initial	Level I Final	Level II Initial	Level II Final	Adsorption % Reduction Level I	Level II
Peanut Hulls (as received)	Hg	112	97	----	----	13.4	----
	Cu	2,475	2,350	12.1	5.7	5.1	52.9
	Ni	325	300	13.3	10.9	7.70	18.0
	Cd	65	60	0.68	0.47	7.70	30.7
	Zn	7,500	6,500	142	110	13.3	22.5
Peanut Hulls (80 Mesh)	Hg	112	87	----	----	22.3	----
	Cu	2,475	2,350	12.1	3.5	5.05	71.1
	Ni	325	300	13.3	11.0	7.69	17.3
	Cd	65	60	0.68	0.32	7.69	52.9
	Zn	7,500	7,000	142	96	6.66	32.4
Peanut Hulls (150 Mesh)	Hg	112	64	----	----	42.9	----
	Cu	2,475	2,250	12.1	2.6	9.09	78.5
	Ni	325	300	13.3	10.9	7.69	18.0
	Cd	65	60	0.68	0.30	7.69	55.9
	Zn	7,500	6,500	142	82	13.3	42.3
Bark (as received)	Hg	112	111	----	----	0.89	----
	Cu	2,475	2,350	12.1	7.5	5.03	38.0
	Ni	325	300	13.3	12.9	7.62	3.01
	Cd	65	61	0.68	0.61	7.59	10.3
	Zn	7,500	6,600	142	138	13.7	2.83
Composted Bark (as received)	Hg	112	105	----	----	6.25	----
	Cu	2,475	2,300	12.1	3.8	7.07	68.6
	Ni	325	310	13.3	10.7	7.64	19.6
	Cd	65	58	0.68	0.50	11.54	26.5
	Zn	7,500	6,400	142	142	13.4	0

metal/g solid, or 11.2% of the total. At lower metal concentrations (similar to municipal wastewater) the retention at one hour dropped to 4.1 mg metal/g solid. However, 24.4% of the metals were removed, with 53% of the copper and 31% of the cadmium adsorbed.

Pine bark was moderately effective in removing Cu from solution, but had little affinity for the other metals. On the other hand, composted bark removed a relatively large percentage of all the metals, with the exception of the low concentration Hg and Zn solutions.

The increased ion-exchange capacity and surface area of composted bark compared to raw bark apparently were responsible for the greater adsorption.

The effect of peanut hull particle size on adsorption for a one-hour exposure is shown in Figure 1. With the exception of nickel, decreasing the particle size significantly increaded the adsorption of each of the metals; the 100-105 micrometer particles removed approximately 20% of the Ni, 40% of the Hg and Zn, 55% of the Cd, and 80% of the Cu from solution.

Summary

The competitive adsorption of common heavy metal ions by peanut hulls, raw bark, and composted bark was studied. These solid wastes were found to adsorb significant amounts of one or more of the heavy metals (Hg, Cu, Ni, Cd, Zn) commonly found in municipal sludge and wastewater.

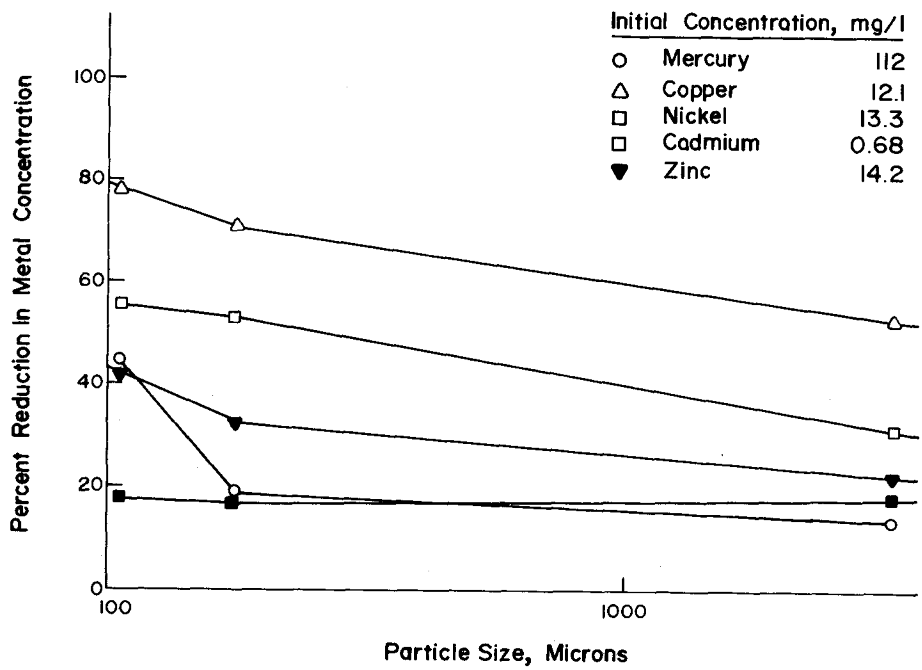

FIGURE I

Effect of Peanut Hull Particle Size on Competitive Adsorption of Heavy Metals.

References

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

BARTH, E.F., M.B. ETTINGER, B.V. SALOTTO, and G.N. McDERMOTT: J. Water Poll. Contr. Fed. 37, 86 (1965).

FRIEDMAN, M., and A.C. WAISS: Environ. Sci. Tech. 6, 47 (1972).

GHOSH, M.M., and P.D. ZUGGER: J. Water Poll. Contr. Fed. 45, 425 (1973).

KING, W.G., J.M. RODRIGUEZ, and C.M. WAI: Anal. Chem. 46, 771 (1974).

LAMB, A., and E.L. TOLLEFSON: Water Res. 7, 599 (1973).

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

McDERMOTT, G.N., W.A. MOORE, M.A. POST, and M.B. ETTINGER: J. Water Poll. Contr. Fed. 35, 227 (1963).

McDERMOTT, G.M., M.A. POST, B.N. JACKSON, and M.B. ETTINGER: J. Water Poll. Contr. Fed. 37, 163 (1965).

MOSHE, M., N. BETZER, and Y. KOTT: Water Res. 6, 1165 (1972).

SMITH, S.B.: Traces of Heavy metals in water - removal processes and monitoring. E.P.A. Report No. 902/0-74-001, Nov. 1973, p.55.