

Binding of Metal Cations by Natural Substances

M. SID MASRI, F. WILLIAM REUTER, and MENDEL FRIEDMAN,
*Western Regional Research Laboratory, Agricultural Research
Service, USDA, Berkeley, California 94710*

Synopsis

The binding of mercuric chloride and other metal salts to bark, activated sludge (Milorganite), chitosan, poly(*p*-aminostyrene), and other natural and synthetic materials was investigated by specific atomic absorption and x-ray fluorescence spectroscopy. The synthetic poly(aminostyrene) was included for comparison with the natural polyamine chitosan. Our results show that a wide range of natural materials are potentially useful for the removal of toxic and precious metals that may be present in industrial effluents, mine waters, or other water supply. Such metal salts include those of mercury, lead, zinc, cadmium, copper, nickel, cobalt, iron, manganese, silver, platinum, palladium, and gold.

INTRODUCTION

In an effort to develop useful scavengers for the removal of mercuric and methylmercuric salts from contaminated sources, we have previously examined the uptake of inorganic and organic mercury derivatives by a variety of synthetic and natural polymers and related model compounds representing different classes of functional groups.¹⁻³ Our results show that proteins such as wool, natural and synthetic polyamine polymers such as chitosan, and tannin-rich agricultural by-products all are effective adsorbents for mercuric and methylmercuric salts. The question arises as to the effectiveness of these materials as potential adsorbents for other toxic metal cations from aqueous systems. Results on the binding of different metal ions by wool have been summarized.⁴ Separation of trace elements from sea water by chromatography on chitosan was reported.⁵ In this report, we compare the binding of some common toxic, precious, and industrial metals to four substrates: bark, activated sewage sludge residue (Milorganite), chitosan, and poly(*p*-aminostyrene). The latter synthetic amino polymer was included for comparison with chitosan, a polymer of glucosamine units of natural origin.

EXPERIMENTAL

Materials Used

Chitosan was prepared by deacetylation of chitin with sodium hydroxide.⁶ We are indebted to Dr. L. Crawford of this laboratory for a gift of chitosan which was used in some of the experiments. Bark (black oak, Douglas fir,

or redwood) was ground (dry) in a Waring blender, stringy fibrous material was discarded, and the remainder was sieved to pass a 20-mesh wire screen (Tyler). Milorganite was purchased in a local nursery, lightly crushed in a mortar, and sieved to pass a 20-mesh screen. The sieved Milorganite (MIL) was washed with distilled water, filtered, dried in an oven, and equilibrated at room temperature and humidity. The washed MIL retained its granular form and lost about 2% weight due to washing. Poly(*p*-aminostyrene) (PAS) came from Polysciences Inc., Rydal, Pennsylvania. Flakes of chitosan (CHT) were used for equilibration without grinding but were ground in a Wiley mill (20-mesh screen) in preparation for metal analysis after equilibration with the metal salt solutions followed by washing and drying. The flakes were a fraction of a millimeter thick and ranged from about 1 to 10 mm² area per flat surface (100 flakes weighed about 0.1 g).

Metal Analysis

The binding of metals by the substrate was measured after equilibration for one day with salt solutions. Generally, 1 g substrate was equilibrated by shaking with 20 mmoles of the salt dissolved in 50–100 ml water. The substrate was then filtered, washed thoroughly with water, air dried, and analyzed for metal content. Untreated substrates were also analyzed to provide control baselines. Three measurements were taken to check metal uptake: (a) weight change of substrate; (b) determination of metal concentration on portions of the dried equilibrated substrates after digestion with nitric acid–potassium permanganate, using specific atomic absorption spectroscopy with a Perkin-Elmer Model 303 spectrometer with an acetylene burner; and (c) direct determination of metal concentration in the equilibrated substrates, using x-ray fluorescence spectroscopy.

X-Ray fluorescence measurements were patterned after the method of Giaque and Jaklevic.⁷ Briefly, the fraction f_i of an element in a sample is expressed as a relationship between the counts in the elemental signal C_i , a matrix correction factor F_i , a single thin-film standard k_j , a fluorescence correction term relating the standard element to the measured element, g_{ij} , and the mass per unit area of the sample (pressed into a thin slide), W_i , so that

$$f_i = \frac{C_i F_i}{k_j g_{ij} W_i} \quad (1)$$

For organic material, F_i , k_j , and g_{ij} need only be determined once with standards. A Qanta/Metrix Model 70 energy dispersive x-ray spectrometer was used for the measurements. Characteristic fluorescence x-rays were excited by the radiation from a filtered rhodium x-ray tube. Fluorescence radiation from K- or L-shell fluorescence was detected for elements lighter and heavier than cesium (atomic number 55), respectively.

The instrumental detection limits are shown in Figure 1. They are calculated from eq. (1) by assuming an elemental signal twice the standard

deviation of the background from a cellulose sample after a 1000-sec measurement.

The detection limit curve is divided into three segments. The upper and lower curved segments respectively are from K- and L-shell x-rays excited by the rhodium K-shell x-rays. The center segment is for elements from Ru to Cs, which are excited by x-ray tube bremsstrahlung emitted at energies greater than the rhodium K-shell x-rays. The loss of sensitivity for the light elements results from air absorption and reduction of x-ray production efficiency. There is a similar loss for the lighter L-shell elements. The peak about element 44 results from the large Compton backscatter peak of the primary rhodium beam. The loss approaching element 55 comes from decreasing bremsstrahlung radiation.

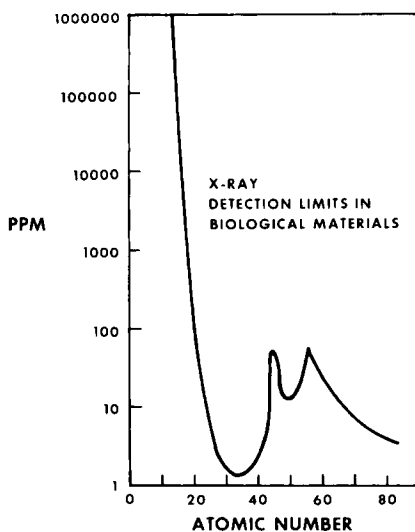


Fig. 1. Metal detection limits in substrates by x-ray fluorescence, with a rhodium target tube for a 1000-sec measurement. K-Shell x-rays are detected from elements lighter than 55, and L-shell x-rays from heavier elements. The fluorescence radiation is excited principally by rhodium K-shell x-rays except elements 44 to 55, which are excited by x-ray tube bremsstrahlung.

Since each of the four substrates was tested for metal uptake individually with one metal salt at a time and since the x-ray fluorescence technique is capable of multielement analysis on the same sample, weighed portions of as many as ten substrates were mixed together to yield one composite sample for x-ray analysis, thus speeding and facilitating measurements considerably. The metal concentration in each substrate was calculated from the measured concentration in the composite sample multiplied by the appropriate dilution factor (1 divided by the weight fraction of equilibrated substrate in the composite sample). In some samples with a high metal content, it was necessary to dilute the substrate with powdered cellulose to bring the metal content down to the valid range of eq. (1), about 20%.

RESULTS AND DISCUSSION

Table I shows the initial (control) levels of various metals in the four substrates as determined by x-ray fluorescence spectroscopy. The versatility and usefulness of this technique for such measurements is obvious, permitting assay of nearly all the metals present above their detection limits in a substrate with a single sample. It is striking that MIL has about 8% iron and considerable amounts of other metals including Ca, Ti, Cr, Cu, Zn, Sr, Zr, and Pb. The relatively high content of metals in MIL may be a reflection of the natural content of metals in the organic matter from which MIL is in part derived, and the affinity of decayed organic matter for metal cations. It may also reflect the nature (composition) of the refuse effluents of a particular community. Comparison of metal analyses of sludge of treated sewage from different locations and periodic analyses on samples of a single location is thus a useful index in assessing metal pollution from natural and industrial sources as well as unusual or transient changes in the composition of metal pollution.

Table II shows the uptake of mercuric chloride by some natural materials. In these experiments, metal uptake by substrate was calculated from the difference between the initial and final concentrations of mercury in solution determined by atomic absorption. It is striking that such materials as dead leaves, bark, top soil, and MIL show relatively high uptake of mercury. Thus, all these materials appear potentially useful for the removal of mercury from the aqueous environment and point to the affinity of mercury to organic matter and earth materials in general.⁸ These

TABLE I
Initial Metal Content (in ppm) of Bark, Milorganite, Chitosan, and Poly(*p*-aminostyrene) Before Equilibration with Salt Solutions by X-Ray Fluorescence Spectroscopy^a

Element	Concentrations in Substrates, ppm						
	Red-wood bark	Douglas fir bark	Black oak bark	Milorganite		Chitosan	Poly-(<i>p</i> -aminostyrene)
				Unwashed	Washed		
Ca	—	12,400	47,200	12,200	9220	5180	—
Ti	—	—	—	5700	3000	—	—
Cr	—	—	—	7760	6440	—	—
Mn	38	340	84	—	—	—	—
Fe	2930	146	574	85,000	81,000	123	107
Ni	9	—	—	—	—	—	11
Cu	26	—	—	508	487	15	9
Zn	128	14	31	1460	740	15	11
Sr	28	77	324	181	150	118	—
Zr	—	—	—	134	121	—	—
Pb	—	—	15	963	963	—	5
Ba	—	—	—	830	810	—	—
Br	—	—	—	—	—	—	71

^a Metals and concentrations shown for each substrate are those which exceed the detection limits in Figure 1.

TABLE II
Mercuric Ion Uptake by Various Substrates^a

Substrate	Hg concn., mg Hg/ml		Calcd. Hg Uptake, ^b mg Hg/g
	Initial	Residual	
Milorganite (H ₂ O)	40	22	460
Milorganite (0.1N HCl)	40	31	225
Bark, Douglas fir	4	2.9	28
Bark, Douglas fir	40	36	100
Bark, redwood	40	30	250
Bark, black oak	40	24	400
Dry redwood leaves	20	13	175
Dry pine needles	20	13	175
Senna leaves	40	30	250
Sulfuric acid lignin	40	38.5	150
Peat moss	20	10.4	240
Orange peel (white inner skin)	4	3.1	23
Orange peel (white inner skin)	20	15	125
Orange peel (outer skin)	4	1.8	55
Orange peel (outer skin)	20	9	275
Chitin	40	36	100

^a With all substrates except lignin, 1 g substrate was equilibrated for one day in 25 ml HgCl₂ (in H₂O; with one indicated exception in 0.1N HCl). With lignin, a ratio of 1 g per 100 ml solution was used.

^b Values calculated by difference between initial and residual concentrations determined by atomic absorption. The treated lignin sample was also analyzed directly by atomic absorption on a portion digested with sulfuric acid-potassium permanganate. Result of this analysis showed 10.8% Hg compared to a value of 13.0% calculated by difference between initial and residual Hg concentration.

substances represent various types of biopolymers rich in proteinacious material, polyamines, lignin-tannin rich substances, and humic acid-type materials.

Table III shows the uptake of various metal cations by four substrates: oak bark, MIL, CHT, and PAS. In these experiments, metal binding was calculated from measurements of metal content of the filtered, water-rinsed, and air-dried substrates. The results are shown as weight per cent metal determined by both x-ray fluorescence on the substrate and by atomic absorption on a digested portion of the substrate. The per cent metal contents and the weights of the equilibrated substrates were used to calculate the binding in terms of millimoles metal per gram (original) substrate. The results, which are given in Table IV, clearly show that

(a) CHT is unique compared to the other substrates: it has higher binding capacity (above 1 mmole/g) with all the metals tested except chromium. CHT formed a liquid gel with concentrated FeCl₃ solution. One gram CHT neutralized 5 mmoles HCl within hours, also forming a gel. One gram also neutralized 5 meq H⁺ from H₂SO₄ (without gelling; CHT gains weight). Thus, hydrogen ion may compete with other cations for binding sites of chitosan.

(b) Although CHT and PAS are both polyamine polymers, they are not equally effective. The greater effectiveness of CHT for metal binding may be due in part to the greater basicity of the aliphatic primary amino group (pK about 10) compared to the aromatic amino group (pK about 5). Nevertheless, PAS bound more than 1 mmole Hg, Cu, Ag, Au, or Pt per gram and 0.9 mmole Pd or 0.5 mmole Zn per gram.

(c) Bark and MIL showed comparable binding with most metals tested. Although their capacity was less than that of CHT, they showed appreciable uptake of many metals including Hg, Pb, Cd, Zn, Cr and others.

TABLE III
Metal Content of Substrates Equilibrated with Aqueous Salt Solutions

Salt	Metal in equilibrated substrates, ^a %			
	Oakbark	Milorganite	Chitosan	Poly- (<i>p</i> -aminostyrene)
HgCl ₂	11.3	13.0	45.5	46.8
HgNO ₃			25.4	
CdCl ₂	2.7	3.2	20	1.1
Pb(NO ₃) ₂	13.6	8.9	42.0	3.4
Pb(C ₂ H ₃ O ₂) ₂			18.8	8.1
ZnCl ₂	4.2	2.4	16.5	3.4
Co(NO ₃) ₂	2.3	0.85	10.2	0.45
NiCl ₂	1.4	0.70	12.8	0.1
Cr(NO ₃) ₃		3.5	2.1	0.13
CuCl ₂	2.3	1.0	13.5	7.2
Fe(NH ₄) ₂ (SO ₄) ₂			6.5	
FeCl ₃	2.6	5.7	^b	0.28
Mn(NO ₃) ₂	0.6		7.1	
AgNO ₃	7.5	5.5	23.7	16.3
AuCl ₃ ·HCl			48.4	39.6
PtCl ₄ ·2HCl	1.4	11	41	36.5
PdCl ₂	9.6	11.4	37.8	8.6
(NH ₄) ₆ Mo ₇ O ₂₄			27.8	3

^a One gram substrate was equilibrated for one day with 20 mmoles salt dissolved in 50–100 ml H₂O, then filtered, rinsed, dried, and weighed. Portions were then analyzed for metal content by x-ray fluorescence and atomic absorption, except for AgNO₃, AuCl₃, PtCl₄, PdCl₂, and (NH₄)₆Mo₇O₂₄, which were measured by x-ray fluorescence only. An average value is cited where both techniques were used.

^b Chitosan liquifies into a gel.

In conclusion, our present and previous results show the potential utility of many natural substances and agricultural by-products as potentially low-cost and readily available substrates for removing and concentrating toxic and other metals from industrial effluents and other water sources (such as in photographic and minewater processing). (For cost potential of chitin, see ref. 9). Finally, it may be feasible to develop a relative affinity series of metal binding to various substrates with the aid of x-ray fluorescence, since this method permits relatively facile multielement assay.

TABLE IV
Metal Binding to Four Substrates from Aqueous Salt Solutions^a

Salt ^b	Uptake, mmole metal/g substrate			
	Bark	MIL	CHT	PAS
Hg	0.62	0.72	5.6	5.70
Cd	0.23	0.29	2.78	0.10
Pb	0.74	0.46	3.97	0.17
Zn	0.63	0.37	3.70	0.52
Co	0.21	0.15	2.47	0.07
Ni	0.22	0.12	3.15	0.02
Cr	—	0.69 ^c	0.46	0.03
Cu	0.35	0.15	3.12	1.31
Fe	0.43	^d	1.18	0.05
Mn	0.10	—	1.44	—
Ag	0.73	0.54	3.26	1.98
Au	—	—	5.84	5.75
Pt	0.06	0.57	4.52	3.82
Pd	0.90	1.18	6.28	0.87
Mo	—	—	3.90	0.31

^a Results were obtained by atomic absorption and x-ray fluorescence. The average of two values was used. See footnote a, Table III.

^b Same as in Table III; with Hg and Pb, data obtained with HgCl₂ and Pb(NO₃)₂ solutions are used.

^c Value corrected for initial Cr content.

^d Not calculated owing to high initial Fe content.

Such series would help in selecting a suitable substrate in situations where there may be competition of various metals for binding sites in the substrate.

The authors are indebted to E. C. Marshall, E. D. Ducay, C. S. Harrison, and Chuckson Yokota for excellent technical assistance.

Reference to a company and/or product name by the Department is only for purposes of information and does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

References

1. M. Friedman and M. S. Masri, *J. Appl. Polym. Sci.*, **17**, 2183 (1973).
2. M. Friedman and A. C. Weiss, Jr., *Environ. Sci. Technol.*, **6**, 457 (1972).
3. M. S. Masri and M. Friedman, *Environ. Sci. Technol.*, **6**, 745 (1972).
4. M. S. Masri, E. D. Marshall, and M. Friedman, Abstracts of Western Regional Meeting of the American Chemical Society, San Francisco, California, October 1972; *Textile Res. J.* (1974), in press.
5. R. A. A. Muzzarelli, G. Raith, and O. Tubertini, *J. Chromatogr.*, **47**, 414 (1970).
6. Q. P. Peniston and E. L. Johnson, U. S. Pat. 3,533,940 (1970).
7. R. D. Giaque and J. M. Jaklevic, *Advan. X-Ray Anal.*, **15**, 164 (1972).
8. U. S. Geological Survey Professional Paper No. 713, *Mercury in the Environment*, U.S. Department of the Interior, U.S. Government Printing Office, Washington, D.C., 1970.
9. U.S. Environmental Protection Agency, Water Pollution Control Research Series 12130 FJQ 06/71, *Pollution Abatement and By-product Recovery*, in *Shellfish and Fisheries Processing* U.S. Government Printing Office, Washington, D.C., 1971.

Received July 24, 1973