Binding of Heavy Metal Ions by Formaldehyde-Polymerized Peanut Skins

JOHN M. RANDALL, EARL HAUTALA, and GARY McDONALD,
*Western Regional Research Laboratory, Agricultural Research Service, U.S.
Department of Agriculture, Berkeley, California 94710*

Synopsis

Peanut skin, when treated with formaldehyde to polymerize tannins, is a highly efficient substrate for removal of many heavy metal ions from aqueous waste solutions. The ions Ag^{1+}, Cd^{2+}, Cr^{6+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, as well as Ca^{2+} and Mg^{2+}, were contacted with formaldehyde-treated peanut skin. Quantitative removal could be achieved with Ag^{1+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}, and Zn^{2+}. Capacity of the substrate for ions was promising for Pb^{2+} (2.1 meq/g substrate), Cu^{2+} (3.0 meq/g), and Cd^{2+} (1.3 meq/g). Sorption from a solution containing Cd^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} on a packed column of formaldehyde-treated peanut skin indicated that Hg^{2+}, Pb^{2+}, and Cu^{2+} were rapidly and completely bound to the packing, while Cd^{2+}, Ni^{2+}, and Zn^{2+} were poorly bound until the preferred ions had been removed from solution.

INTRODUCTION

The removal of toxic heavy metal ions from sewage and from industrial and mining waste streams has received much attention in recent years. Precipitation and ion exchange represent two removal techniques which are often adequate to remove heavy metals from solution. Synthetic ion exchange resins are, however, often quite expensive.

Many agricultural waste materials act as natural ion exchange or chelating agents and are usually available at little or no cost. The removal of mercuric ion solution by contact with agricultural wastes has been reported by Friedman and Waiss,[1] binding of mercury and other metal ions with varied organic wastes by Masri, Reuter, and Friedman,[2] binding of heavy metal ions on wool by Masri, Reuter, and Friedman,[3] and binding of a number of heavy metals on various barks by Randall, Bermann, and Waiss.[4] Peanut skin (testa), an inexpensive, tannin-containing agricultural waste product from the roasting and packaging of Virginia peanuts, has been reported to be effective in removing cupric ion from solution.[4]

However, raw peanut skin has two disadvantages for use as a natural adsorbent or ion exchange substrate. First, on contact with water, there is initial leaching of reddish color into solution. The soluble colored compounds are primarily low molecular weight tannins. Second, on prolonged contact with water, peanut skins tend to disintegrate. In order to overcome these problems, raw peanut skins were treated with hot, acidified, aqueous formaldehyde to condense the tannins and thus insolubilize the colored compounds. The polymerized material was tough, quite stable in contact with water, and was as effective in binding cupric ion as was raw peanut skin.[5]

Besides copper, there are numerous other heavy metal ions which are toxic

0021-8995/78/0022-0379$01.00

or are not desirable in waste streams for other reasons. Among them are Ag^{1+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cr^{6+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}. Some of these ions are easily removed below current EPA or local water quality limits by conventional methods,[6] but others present either technical or economic problems. Since peanut skin removes cupric ion so completely from solution, probably by complexing of the tannin molecules with Cu^{2+}, this paper will investigate use of formaldehyde-treated peanut skin as a natural ion exchange material to bind other heavy metal ions.

EXPERIMENTAL

Adsorbent

Fresh, raw peanut skins, the basic material used for this study, were formaldehyde-treated by immersion of 1 part peanut skin (weight) in approximately 10 parts of $0.2N$ H_2SO_4 containing 2% formaldehyde at 50°C for 2 hr (FTPS). Details of the procedure are given by Randall, Reuter, and Waiss.[4] The treated peanut skins were washed with water and oven dried at 40°C to approximately 4% moisture. For experiments with small columns and for all equilibrium tests, treated skins were ground in a Wiley mill to pass through a 1-mm screen (DGFTPS). This was done in order to increase surface area and to reduce wall effects in small packed columns.

Equilibrium experiments were carried out by combining 1 part of peanut skin with 100 parts of solution and agitating for several hours in a glass-stoppered

TABLE I
Removal of Heavy Metals from Solution—Equilibrium Experiments[a]

| Metal compound | Cation concentration in solution | | | | pH | |
| | Initial | | Final | | | |
	ppm	meq/l.	ppm	meq/l.	Initial	Final
AgNO$_3$	95	0.88	72	0.67	4.0	3.6
AgOAc	44	0.41	17.5	0.16	—	4.4
	80	0.71	31	0.27	—	4.45
	174	1.61	58.5	0.54	—	4.5
Ca(NO$_3$)$_2$	20.5	1.03	13.3	0.67	6.21	3.03
Ca(OAc)$_2$	21.0	1.05	8.4	0.42	6.17	3.30
Cd(NO$_3$)$_2$	100	1.78	30	0.53	5.2	3.15
	90	1.60	5.0	0.089	5.0	—
Cd(OAc)$_2$	100	1.78	7.8	0.14	6.0	3.9
K$_2$CrO$_4$	100 (Cr^{6+})	—	63 (Cr^{6+})	—	—	—
CuCl$_2$	50	1.57	4.7	0.15	5.90	3.25
Cu(OAc)$_2$	50	1.57	0.42	0.013	5.95	5.60
Mg(NO$_3$)$_2$	12.0	0.99	10.9	0.90	—	—
Mg(OAc)$_2$	12.0	0.99	9.3	0.76	—	—
Ni(NO$_3$)$_2$	55	1.87	35	1.19	5.78	3.00
Pb(NO$_3$)$_2$	100	0.97	1.9	0.035	4.8	3.1
Pb(OAc)$_2$	100	0.97	0.7	0.0067	5.1	3.6
Zn(NO$_3$)$_2$	31.9	0.78	10.4	0.32	5.83	3.09
Zn(OAc)$_2$	21.8	0.67	1.6	0.049	6.08	3.70

[a] One part substrate contacted with 100 parts solution (weight).
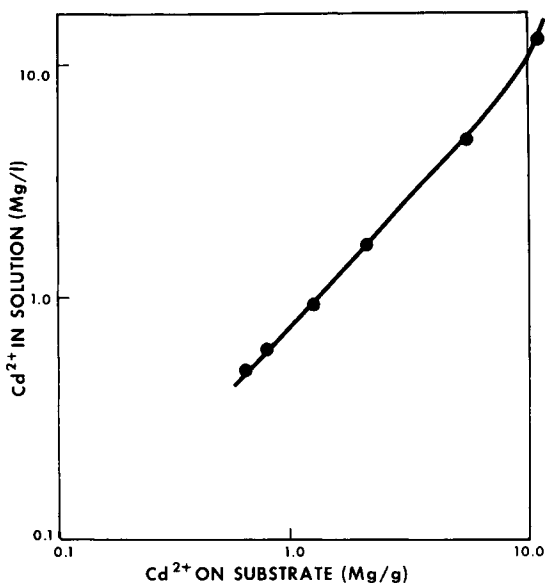
Fig. 1. Adsorption isotherm for adsorption of cadmium ion from cadmium acetate solution on formaldehyde-treated peanut skins.

Erlenmeyer flask. The mixture was filtered and the solid dried at 40°C for 24 hr if it was to be analyzed for heavy metal.

Sections of 20-mm-ID glass pipe, 25, 50, or 100 cm long, were used for packed columns. Adsorbent was placed dry into the column and the column tapped very gently to promote even distribution of packing in the column. The packing density of DGFTPS in the columns was approximately 0.15 g/cm³. Glass beads were added on top of the packing to prevent the adsorbent particles from floating and to prevent the column from separating. The packing was wetted with a slow water flow, either upflow or downflow, and was equilibrated for several hours, filled with water. Flow of test solutions through the column was always by gravity, controlled by a valve at the bottom of the column.

TABLE II
Removal of Heavy Metals from Solution on DGFTPS Columns

Cation	Ag^{1+}	Cd^{2+}	Cu^{2+}	Ni^{2+}	Pb^{2+}
Compound	$AgNO_3$	$Cd(NO_3)_2$	$CuSO_4$	$NiCl_2$	$Pb(NO_3)_2$
Cation concn. in feed, ppm	197	11	23	20	22
Flow rate, bed vol/hr	1.91	4.3	1.4	3.7	1.2
Total feed, g cat/g packing	0.081	0.0296	0.0547	0.0095	0.048
Feed at steady state, g/g	0.025	0.0246	0.0208	0.0039	0.048
Feed at steady state, meq/g	0.232	0.440	0.635	0.132	0.464
SS concn of cation in eff., ppm	0.01	0.02	0.03	0.1	0.05
Total cation bound, g/g	0.0688	0.0290	0.033	0.0092	0.048
Total cation bound, meq/g	0.637	0.518	1.01	0.0038	0.464
Concn of cation at top of packing, g/g	—	0.0408	—	—	0.159
Concn of cation at top of packing, meq/g	—	0.729	—	—	1.54
pH of steady-state effluent	3.9	4.6	3.6	3.4	4.0

Analysis

Solid. All solid adsorbent samples were analyzed with an energy-dispersive x-ray fluorescence spectrometer developed by Quanta/Metrix, a division of Finnegan Corporation, Sunnyvale, California.[7] In this nondestructive technique, a wafer of material is subjected to a beam of rhodium K x-rays. The excited fluorescence x-ray spectrum is detected and stored as a function of energy. Quantitative analysis of all the heavy metals in the sample is obtained from one spectrum by a method described by Reuter and Reynolds.[8]

Liquid. Liquid samples were analyzed primarily with a Perkin–Elmer 303 atomic absorption spectrometer. Frequent mass balances were performed with the x-ray fluorescence results to ensure that the total amount of copper in the feed solution was accounted for in the column effluent and solid adsorbent. A few liquid effluents were analyzed by x-ray fluorescence by drying the liquid on cellulose powder. In general, however, atomic absorption spectroscopy was found to be faster and more sensitive than the x-ray fluorescence method.

RESULTS AND DISCUSSION

Batch Adsorption Tests

Simple experiments were carried out by contacting peanut skin (DGFTPS) with solutions of heavy metal ions and agitating until equilibrium was attained. Since the substrate acts as an acid-form ion exchanger, releasing hydrogen ion into solution as metal ions are bound, the equilibrium attained is that corresponding to a solution at a lower pH than that of the original test solution. Previous work has established that efficiency of metal binding on FTPS increases with increasing pH, at least to the pH where the metal ions may precipitate from

TABLE III
Removal of Pb^{2+} from Lead Acetate Solution on a Packed Column of Formaldehyde-Treated Peanut Skin, Including Regeneration of Substrate and Subsequent Use[a]

	I[b]	R	S
Compound	$Pb(OAc)_2$		$Pb(OAc)_2$
Cation concn in feed, ppm	320		300
Flow rate, bed vol/hr	1.2		1.0
Total feed, g Pb^{2+}/g substrate	0.132		0.111
Feed at steady state, g/g	0.078		0.073
Feed at steady state, meq/g	0.761		0.71
Steady-state concn of cation in effluent, ppm	0.2		0.2
Total cation bound, g/g	0.101		0.093
Total cation bound, meq/g	0.98		0.90
Concn of cation at top of packing, meq/g	—		2.08
pH of steady-state effluent	3.8		3.8
Eluent		HCl, 0.1N	
Total eluent, ml		300	
Max. concn of Pb^{2+} in eluent, ppm		8500	

[a] Packing was 20.4 g of DGFTPS, 44 cm in height, in a 20-mm-ID glass column.
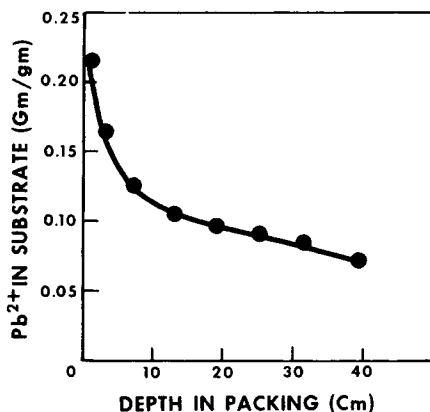[b] I = initial adsorption experiment; R = regeneration step; S = second adsorption experiment.

Fig. 2. Concentrations of lead in a packed column contacted with lead acetate solution.

solution.[5] Thus, these simple equilibrium tests cannot establish the maximum sorptive capacity of FTPS, but they do serve to indicate whether a particular metal ion is strongly bound or only weakly bound on FTPS.

Variation in binding of different metal ions is especially noticeable if the heavy metal solution is somewhat buffered by the use of a metal acetate instead of a nitrate or chloride salt. Results for a number of heavy metal ions, some with different anions, are given in Table I. It is quite apparent that for some metal ions, sorption improved dramatically in acetate solution as compared to nitrate solution. For example, a solution of 100 ppm Cd^{2+} as nitrate was decreased to 30 ppm after contact with peanut skin, while a solution of 100 ppm Cd^{2+} as acetate was decreased to 7.8 ppm. Similar improvements in binding with buffered solution can be seen for other metals, including silver (Ag^{1+}), calcium (Ca^{2+}), copper (Cu^{2+}), lead (Pb^{2+}), and zinc (Zn^{2+}). As would be expected, the final solution pH in the acetate solution was always higher than for nitrate or chloride solution.

The results of Table I indicate that peanut skin should be effective in binding Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} and perhaps Ag^{1+}, Ni^{2+}, and Cr^{6+}. Calcium (Ca^{2+}), Co^{2+}, and Mg^{2+} were not bound well. These results provided a basis for further work on nonequilibrium tests with packed beds.

TABLE IV
Maximum Capacity of Formaldehyde-Treated Peanut Skin for Heavy Metal Ions[a]

	Cd^{2+}	Cu^{2+}	Cu^{2+}	Pb^{2+}
Heavy metal compound	$Cd(OAc)_2$	$CuSO_4$	$Cu(OAc)_2$	$Pb(NO_3)_2$
Concn of M^{2+} in feed, ppm	100	33	50	100
Total M^{2+} fed to column, g	3.0	0.7	1.1	3.6
Max. concn of M^{2+} on packing, mg M^{2+}/g substrate	74	51.5	96	205
Max. concn of M^{2+} on packing, meq M^{2+}/g	1.32	1.62	3.0	1.97

[a] 20-mm-ID glass column packed with 12 g DGFTPS.

Effect of Metal Ion Concentration

The results of Table I were mostly obtained by contacting a metal ion (M^{2+}) solution of arbitrary concentration with DGFTPS. The results would change as the original M^{2+} concentration in solution changed. As the initial metal concentration increased, absolute removal of metal ion from solution would increase, but percentage removal would decrease. The effect of initial M^{2+} concentration on the final concentration would be present for both buffered and unbuffered solutions, but it would be less apparent for metal acetate solutions, where the increase in hydrogen ion concomitant with ion exchange would not inhibit binding of heavy metal ions. An adsorption isotherm for binding of Cd^{2+} from $Cd(OAc)_2$ solution on DGFTPS is given in Figure 1. This is a typical adsorption isotherm for such a reaction and corresponds with a similar one for Cu^{2+} previously published.[5]

Nonequilibrium Tests

A continuous sorption of heavy metal ions on a packed bed of peanut skin would provide a much better indication of the capacity of the substrate for binding an ion. Also, continuous sorption on a packed bed is often more economical to operate than a batch process. Adsorption in a packed column is inherently a nonequilibrium process, although under certain conditions nearly steady state operation can be achieved. For low liquid flow rates, the process approximates equilibrium from point to point in the column.

Table II gives results for several experiments of removal of heavy metal ions from solution on packed beds of DGFTPS. All of the metals tested were almost completely removed from solution, at least for a short time. The greatest apparent capacity of DGFTPS for removal of metal ions was for Cu^{2+}. Before the column broke through (Cu^{2+} began to appear in the effluent from the column), 0.635 meq Cu/g substrate was bound on the packing overall, which compares to 0.440 for Cd^{2+}, 0.232 for Ag^{1+}, and only 0.132 for Ni^{2+}. Only 0.464 meq/g Pb was taken up overall, but the column never broke through, and the ultimate capacity at breakthrough is unknown.

The actual binding capacity of Pb^{2+} on peanut skin is better shown by the results shown in Table III. In this case, the feed was $Pb(OAc)_2$, about 300 ppm Pb^{2+}. Sufficient Pb^{2+} solution was passed through the column in step I to ensure breakthrough. "Steady-state" concentration of Pb^{2+} in the column effluent was less than 0.2 ppm and probably less than 0.05 ppm, although at the time, the lowest lead concentration that could be measured was 0.2 ppm. After the sorption experiment was completed, the packing was regenerated (step R) by passing 300 ml of 0.1 N HCl through the column to elute lead ion from the packing and regenerate the hydrogen form of the ion exchanger. The peanut skin substrate, which turned brownish black as Pb^{2+} was sorbed, immediately returned to its original orange color as the acid eluted Pb^{2+} from the packing. The regenerated packing was washed with water to remove excess acid. The use of HCl was a mistake, for $PbCl_2$ has limited solubility in water. This produced some zone precipitation in the column and limited the concentration of lead in the eluate (8500 ppm). Nitric acid would have been a more efficient strong acid to elute lead from the packing, as has been verified for other sub-

strates.[4] Because of the zone precipitation, the packing may not have been completely stripped of lead ion.

The second sorption experiment is shown in step S. A lead acetate solution similar to that of step I was passed through the column. The quantity of lead ion sorbed by the packing before breakthrough was about 94% of that of the initial sorption run (0.073 g Pb^{2+}/g substrate, compared to 0.078 originally), and this probably reflects the difficulty encountered in completely eluting Pb^{2+} with HCl rather than an actual diminished capacity of the substrate. Prior to breakthrough, 0.71 meq Pb/g substrate was bound on the column, and a total of 0.90 meq Pb/g substrate was bound when the feed was discontinued. After the lead feed was discontinued, the packing was washed with water, drained, and cut into segments and dried for analysis of Pb by x-ray fluorescence. The results are shown in Figure 2. The maximum concentration of lead in the substrate (0.215 g Pb/g substrate) occurred, as expected, at the point where the fresh feed entered the column. The concentration then tailed off to 0.075 g/g at the outlet of the column. This concentration of Pb was relatively high, and the entire curve somewhat flattened out, because feeding of lead solution was continued for some time after breakthrough.

In order to determine the maximum capacity of a peanut skin substrate for several of the heavy metal ions, short packed columns of peanut skin were treated with large quantities of heavy metal solution, far in excess of the volume required to produce breakthrough as determined by the data from Tables II and III. This was designed to saturate the entire column and to virtually eliminate to usual concentration gradient in a packed column. This was reasonably successful. For instance, for a column treated with Cd^{2+} solution, the top of the packing contained 0.074 g Cd/g substrate at the end of the experiment, as compared to 0.062 at the bottom of the packing. Results for Cd^{2+}, Cu^{2+}, and Pb^{2+} are given in Table IV. The results represent at least an approximation of the absolute capacity of peanut skin for these metal ions.

Competition Among Metal Ions

Formaldehyde-treated peanut skin can effectively bind a number of heavy metal ions, but it would be doubtful if all ions were bound equally tightly; and considering the peanut skin is a complex material with many possible binding sites, it is quite possible that not all ions are bound in the same sites or even by the same mechanism. In order to determine how well metal ions are removed from solution in direct competition with other heavy metals, a column was packed with DGFTPS (30 g) and contacted with a solution containing approximately 10 ppm each of Cd^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} and 6 ppm of Ni^{2+}. The solution was fed to the column until breakthrough had occurred for Ni^{2+}, Zn^{2+}, and Cd^{2+} (in that order). The feed was discontinued, the column washed with water and drained, and the packing cut into 2-cm sections and dried for heavy metal analysis. The results of metal analysis are given in Figure 3 in terms of meq M^{2+}/g substrate, in order to more clearly illustrate the relative binding capacity for the various metal ions in competition with other metal ions.

Lead, mercury, and copper were all bound well by the packing. There is some indication that these ions are removed from solution by several independent mechanisms. Mercury is probably not removed by ion exchange or chelation
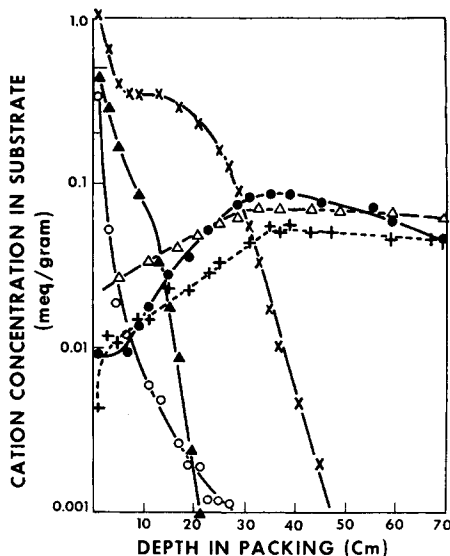
Fig. 3. Concentration profiles of six metal ions sorbed from a solution by contact with a packed bed of peanut skin: (●—) Cd; (×—) Cu; (○—) Hg; (+ - - -) N; (▲—) Pb; (△ - -) Zn.

but by reduction to mercury metal, which is then physically attached to the surface of the substrate. This is supported by the fact that in batch contacting of Hg^{2+} solution and peanut skin in a flask, the walls of the flask were silvered if the flask was violently agitated during the contact period. Cadmium, nickel, and zinc concentrations seemed to be inversely related to the lead concentration but not strongly related to copper concentration. This would suggest that lead, cadmium, nickel, and zinc are primarily bound by one mechanism but that copper is partly bound by another mechanism. Since the concentration of bound cadmium, nickel, and zinc did not achieve maximum levels until the copper concentration fell to zero, there may have been some interaction between these metal ions and copper. Lastly, the copper and lead concentrations through the column seem to be relatively independent of each other.

The metal ions were added in units of weight concentration (ppm) and not in units of molar concentration. Thus, the relative metal concentrations on the peanut skin substrate of Figure 3 do not represent a mass action competition, but they are sufficient to indicate differences in M^{2+} binding affinity.

CONCLUSIONS

Formaldehyde-treated peanut skin is an excellent substrate for the sorption and quantitative removal of a number of heavy metal cations from aqueous solution. The concentrations of Cu^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} in waste streams can be reduced to levels well below existing federal and local waste water quality standards. The binding capacity of peanut skin is quite high for Cd^{2+}, Cu^{2+}, Hg^{2+}, and Pb^{2+} and is competitive with that of many synthetic ion exchange resins, well above 1 meq metal/g substrate. Treatment of aqueous waste streams with peanut skin offers a promising, inexpensive means of meeting stringent water quality standards.

References

1. M. Friedman and A. C. Waiss, Jr., *Environ. Sci. Technol.*, **6**, 457 (1972).
2. M. S. Masri, F. W. Reuter, and M. Friedman, *J. Appl. Polym. Sci.*, **18**, 675 (1974).
3. M. S. Masri, F. W. Reuter, and M. Friedman, *Text. Res. J.*, **44**, 298 (1974).
4. J. M. Randall, R. Bermann, V. Garrett, and A. C. Waiss, Jr., *Forest Prod. J.*, **24**, 80 (1974).
5. J. M. Randall, F. W. Reuter, and A. C. Waiss, Jr., *J. Appl. Sci.*, **19**, 1563 (1975).
6. J. C. Dean, F. L. Bosqui, and K. H. Lanouette, *Environ. Sci. Technol.*, **6**, 518 (1972).
7. W. G. Wood, *Ind. Res.*, **14**, (10), 38 (1972).
8. F. W. Reuter and W. Reynolds, *Biology Ser.*, **48**, 621 (1974).