Effect of Light Metal Ions on the Sorption of Heavy Metal Ions on Natural Polymers

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Synopsis

Dried ground formaldehyde-treated peanut skins, white ash bark, and So. Wisconsin red maple bark are efficient substrates for removal of many heavy metal ions from waste streams, but possible interference by common light metal cations has never been determined. The influence of Ca^{2+}, Mg^{2+}, or Na^+ on the removal of the heavy metal ions Pb^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+} by the above substrates was studied in both batch and packed-column experiments. It was found that Pb^{2+} and Cu^{2+} were minimally affected by the presence of these light metal ions in solution, while the uptake of Cd^{2+} and Zn^{2+} was significantly reduced. Calcium ion produced the greatest effect of the light metals tested.

INTRODUCTION

Previous research has shown that many agricultural waste products act as inexpensive natural ion exchange or chelating agents which are effective in removing toxic heavy metal ions from industrial and mining waste streams and sewage. The removal of mercuric ion from solution by contact with agricultural wastes has been reported by Friedman and Waiss,[1] and the binding of Hg^{2+} and other metal ions with various organic wastes, by Masri, Reuter, and Friedman.[2] Binding of heavy metal ions on wool was reported by Masri, Reuter, and Friedman,[3] binding of several heavy metals on various barks and raw peanut skins, by Randall, Berman, Garret, and Waiss,[4] and binding of cupric ion and other metal ions on formaldehyde-treated peanut skins, by Randall, Hautala, and McDonald.[5]

A proposed mechanism for metal binding is chelation of divalent metal ions on the catechol-type rings in the polymeric tannin structure found in significant amounts in many agricultural wastes. Evidence for this statement rests on some electron spin resonance experiments comparing copper–catechol chelates with copper–peanut skin complexes. Both showed the same pattern, indicating that copper may bind to peanut skin in the same manner that it binds to catechol. However, the mechanism has not been definitely proved.

It has been tacitly assumed that light metal ions such as Na^{2+}, Mg^{2+}, and Ca^{2+}, which may be present in high concentrations in some waste streams (e.g., sea water wastes), are only minimally sorbed by the natural substrates and do not seriously interfere with the removal of potentially toxic heavy metal ions from solution. However, some preliminary experiments have shown that certain

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natural polymers used as ion exchangers for heavy metal ions can sorb significant amounts of Ca^{2+} and Mg^{2+}.[6]

Possible interferences by Ca^{2+}, Mg^{2+}, and Na^+ on the sorption of Pb^{2+}, Cu^{2+}, Cd^{2+}, or Zn^{2+} by several natural ion exchange substrates (dried ground form-aldehyde-treated peanut skins, white ash bark, and So. Wisconsin red maple bark) are investigated in this paper. Of special concern are situations in which a light metal ion is present in high concentration compared to the heavy metal ion.

EXPERIMENTAL

Dried ground formaldehyde-treated peanut skins (TPS) were prepared from fresh raw peanut skins (obtained from Planters Peanuts) by immersion of one part by weight peanut skins in approximately 10 parts $0.2N$ H_2SO_4 containing 2% formaldehyde, at 50°C for 2 hr. Details of this procedure are given by Randall, Reuter, and Waiss.[7] Treated skins were ground in a Wiley mill to pass a 1.0-mm screen in order to increase surface area.

White ash (WAB) and So. Wisconsin red maple (RMB) barks (obtained from U.S.D.A. Forest Products Lab., Madison, Wisconsin) were dried at 60°C for 24 hr and ground in a Wiley mill to pass a 1.0-mm screen.

A series of stock metal solutions for batch and column experiments were prepared with analytical reagent-grade nitrates of Na, Mg, Ca, Cu, Zn, Cd, and Pb in glass-redistilled water. These solutions were prepared to contain the heavy metal alone or in combination with one of the light metal ions.

Batch equilibrium experiments were carried out by combining 1.0 g substrate with 100 ml of a metal solution in a 125-ml glass-stoppered Erlenmeyer flask and agitating intermittently for 24 hr. The test solutions always contained 0.5 meq/l. of the heavy metal ion to be studied, with varying concentrations of a light metal ion. After equilibration the mixture was filtered and the filtrate analyzed for heavy metal ion concentration.

Packed-column experiments were run in 12-mm-I.D. glass columns. The substrate (8 g TPS or 12 g WAB) was placed dry into the column. The column was tapped gently to promote even distribution of the packing. The density of the packed substrate was approximately 0.2 g/cm^3 for TPS and 0.3 g/cm^3 for WAB. Glass beads (3 mm) were placed on top of the substrate to prevent sep-aration of the column and to keep substrate particles from floating. The height of each packed column was 37–40 cm. The column was equilibrated with a slow upflow of water for 1 hr to completely wet the substrate and to eliminate air bubbles before introduction of the metal feed solution. Flow of solutions was upflow by gravity feed, controlled by a stopcock at the bottom of the column. Flow rates ranged from 0.5 to 2.5 ml/min, and feed volume was approximately 2 liters. Column effluent samples were analyzed periodically only as a check on running conditions and are not reported. Upon completion of runs, columns were washed with water and drained. Substrates were divided into 1- to 3-cm sections of column length, dried at 60°C in a forced air oven for 16 hr, and saved for metal analysis of solids.

ANALYSIS

Liquids

Feed and effluent solutions from column experiments and filtrates from batch tests were analyzed using a Perkin-Elmer Model 303 atomic absorption spectrophotometer (Perkin-Elmer Corp. Norwalk, Conn.), using standard conditions described by Perkin-Elmer.[8]

Solids

Dried substrate sections were analyzed with a Finnigan Model 80 energy dispersive x-ray fluorescence spectrometer (Finnigan Corp. Sunnyvale, Calif.), using techniques developed by Reuter and Raynolds.[9] Reduction of raw data was performed on an IBM 1800 computer, using a FORTRAN program to correct for matrix and interelement effects.[10]

RESULTS AND DISCUSSION

Batch Sorption Tests

Equilibrium batch tests were run to determine the general effect different light metal ions have on the sorption of various heavy metal ions by natural substrates. A batch test is not as efficient as a column run, but is a simple, effective method for determining gross effects. These results were used as a screening method to indicate which nonequilibrium packed-column tests would be of most interest.

The results of a number of batch tests on the three substrates are given in Figures 1 to 4. These figures show the percent uptake of the heavy metal alone compared to the uptake of the heavy metal when a light metal was also in the feed solution.

Results of some batch tests using TPS as the substrate are shown in Figure 1. The light metals Ca^{2+}, Mg^{2+}, and Na^+ in concentrations of 5, 10, and 30 meq/l., respectively, are shown in competition with 0.5 meq/l. of the heavy metals Pb^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+} and are compared to the uptake of the heavy metal ion alone. The most readily sorbed heavy metal in Figure 1 was Pb^{2+}, with an uptake of 95%; it was also the least affected by the presence of a light metal ion in solution, with the percent uptake being about 96%, 93%, and 90% for Ca^{2+}, Mg^{2+}, and Na^+ interferences, respectively. Copper uptake was also slightly affected by the light metal ions Ca^{2+} and Mg^{2+}, with 93% uptake of copper alone compared to about 87% and 90% for Ca^{2+} and Mg^{2+}, respectively. Sodium had a slightly stronger effect, reducing uptake to about 76%. Cadmium and zinc ions were sorbed less effectively than were Pb^{2+} and Cu^{2+} on TPS. These ions (Cd^{2+} and Zn^{2+}) also showed decreased sorption in the presence of light metal ions. Uptake of Cd^{2+} dropped from about 79% to about 43%, 54%, and 61% in the presence of Ca^{2+}, Mg^{2+}, and Na^+, respectively, in the solution. Uptake of Zn^{2+} (68%) was reduced to about 42%, 40%, and 48% in the presence of Ca^{2+}, Mg^{2+}, and Na^+, respectively. Treated peanut skins would be an acceptable substrate for removal of Cd^{2+} and Zn^{2+} from solution only if light metal ions were absent or were present in much lower concentrations than shown in Figure 1.
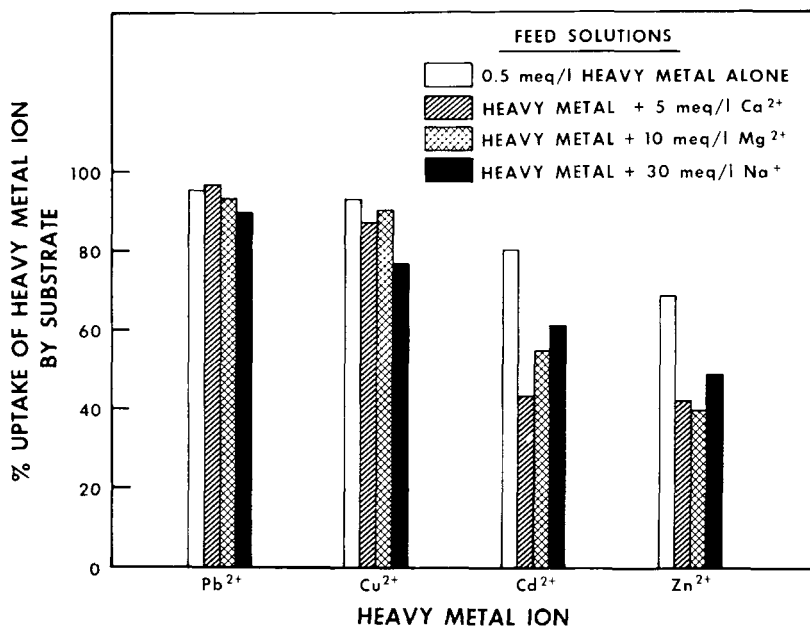
Fig. 1. Sorption of heavy metal ions on TPS substrate in batch tests.
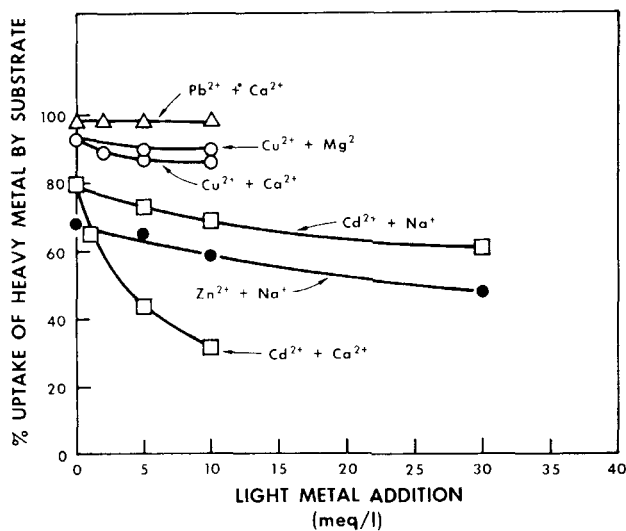

Fig. 2. Effect of increasing light metal ion concentration on heavy metal uptake by TPS.

It has been assumed that as light metal ion concentration increases, interference effects become more pronounced. This was verified for some metal ion combinations using TPS substrate as shown in Figure 2. The sorption of lead and copper ions was relatively unaffected by increasing light metal concentration. Cadmium and zinc ions, which showed the greatest susceptibility to light metal interference in Figure 1, were moderately affected by increasing Na^+ concentration. Cadmium uptake was reduced by half as the Ca^{2+} concentration increased over the range of 0 to 10 meq/l. Ca^{2+}.

Results of batch tests with white ash bark as the substrate are shown in Figure
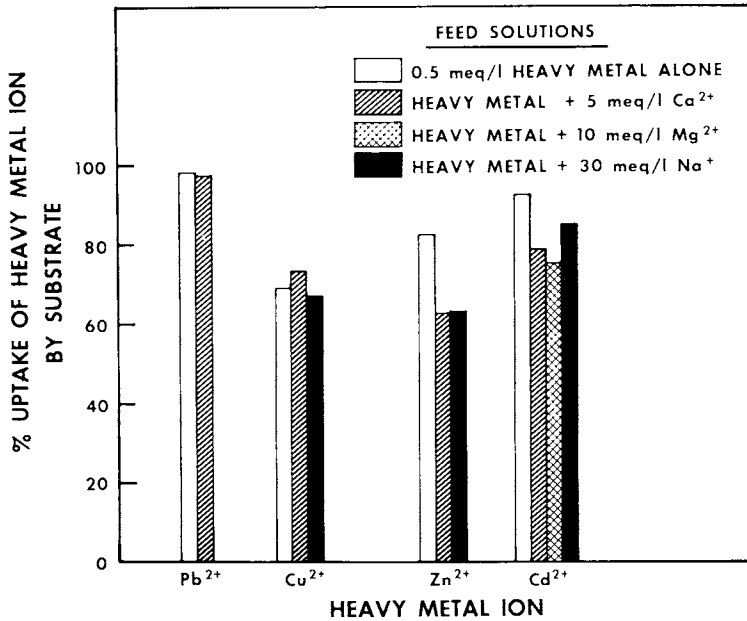
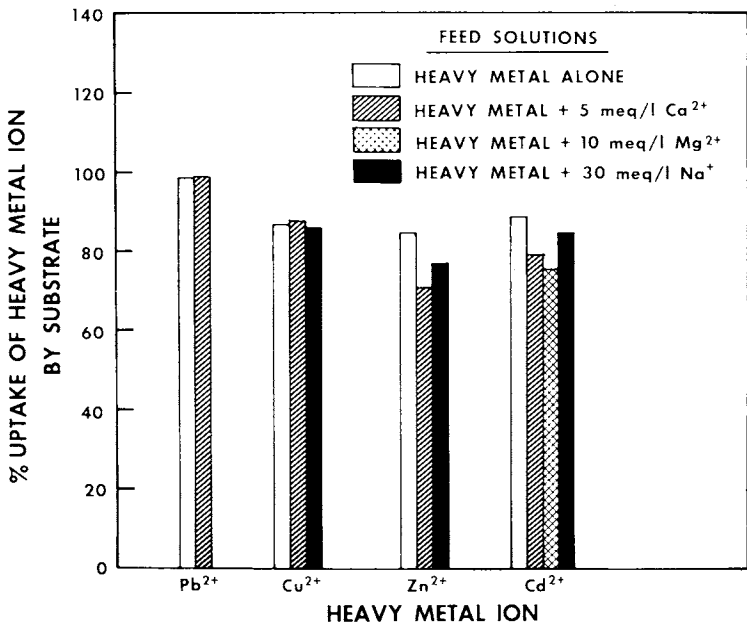Fig. 3. Sorption of heavy metal ions on WAB substrate in batch tests.

Fig. 4. Sorption of heavy metal ions on RMB substrate in batch tests.

3. Lead ion was readily sorbed on the substrate (98% uptake) and was unchanged by the presence of 5 meq/l. Ca^{2+} in the solution. The sorption of Cu^{2+} on WAB was only 69%, but the presence of light metal ions had little influence. The uptake of Cu^{2+} actually increased to 73% in the presence of 5 meq/l. Ca^{2+}. Uptake of Cd^{2+} was higher (94%) on WAB than on TPS, while interference by light metal ions was not as great. Zinc uptake on WAB was also higher than on

TPS. However, the light metal effects were about the same as on TPS. From these results it can be seen that for removal of Cd^{2+} from solution, WAB is a more efficient substrate than TPS. For Cu^{2+} removal, TPS would be a better substrate than WAB.

Another bark, So. Wisconsin red maple (RMB) (Fig. 4) showed results similar to those for WAB except that Cu^{2+} uptake was higher (87%) and Ca^{2+} and Na^+ interfered less with Cd^{2+} and Zn^{2+} uptake than they did on WAB substrate.

Column Sorption Tests

Continuous sorption of metal ions on a packed column is more economical than batch tests and gives a better indication of the actual binding capacity of the substrate. While sorption on a packed column is inherently nonequilibrium, at low flow rates the process approximates equilibrium from point to point on the column.

Batch tests showed that Ca^{2+} generally interfered more with heavy metal ion uptake than did the other light metals tested; all column experiments were carried out with Ca^{2+} as the light metal ion.

Figures 5 to 7 show results of columns run with TPS as the substrate. In these figures metal ion concentrations were plotted as a function of distance from column inlet. Two columns were run with Cd^{2+} as the heavy metal (Fig. 5). In one column, 0.5 meq/l. Cd^{2+} was run as a control with no interfering light metal ion. In the second column, the feed solution contained 0.5 meq/l. Cd^{2+} plus 2.5 meq/l. Ca^{2+}. As had been indicated by batch tests, uptake of Cd^{2+} was greatly reduced by the presence of Ca^{2+}. The control column showed an ionic capacity (highest concentration found on the substrate) of 0.32 meq Cd^{2+}/g substrate. With Ca^{2+} present in the feed solution, only 0.085 meq Cd^{2+}/g was sorbed on the first substrate section while the total ionic capacity (Cd^{2+} + Ca^{2+}) was only slightly less (0.28 meq cation/g) than the uptake of Cd^{2+} alone. This indicates that rather than significantly reducing the ionic capacity of the column, Ca^{2+} competes successfully with Cd^{2+} for sorption sites on the substrate.
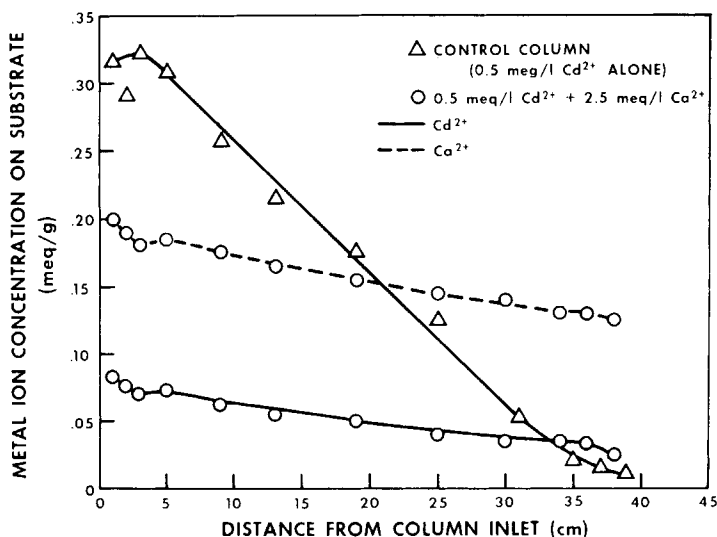

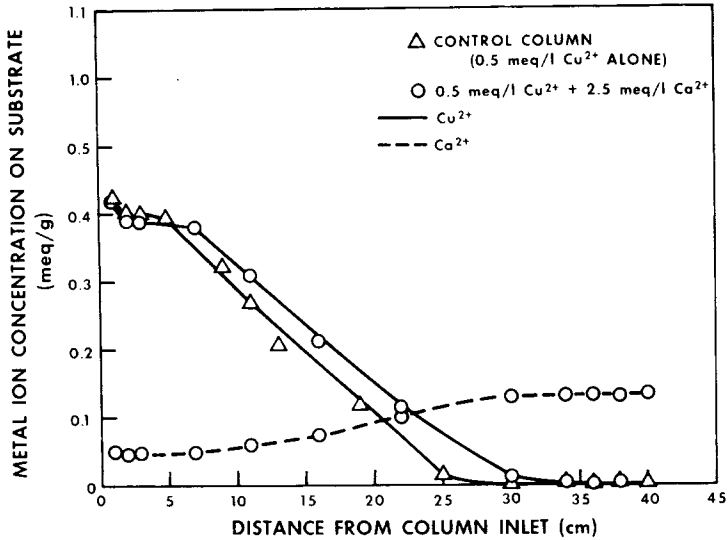Fig. 5. Distribution of Cd^{2+} and Ca^{2+} on TPS substrate in packed-column tests.

Fig. 6. Distribution of Cu^{2+} and Ca^{2+} on TPS substrate in packed-column tests.
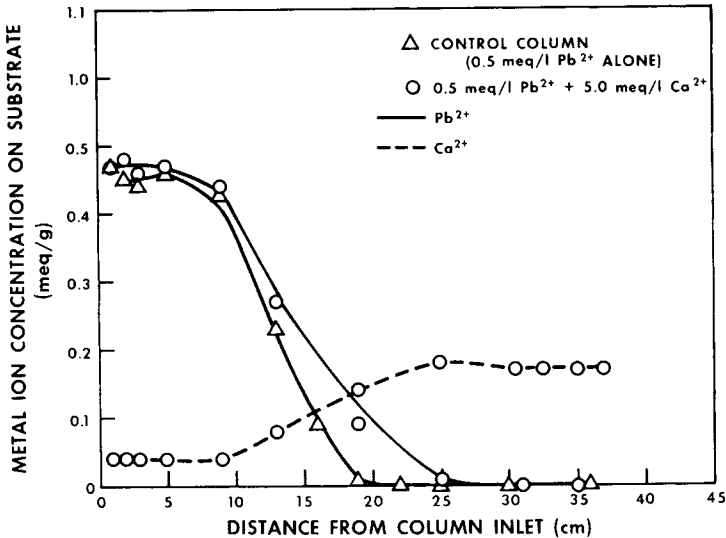

Fig. 7. Distribution of Pb^{2+} and Ca^{2+} on TPS substrate in packed-column tests.

The two columns run on TPS with Cu^{2+} as the heavy metal are shown in Figure 6. Data showing that the capacity of TPS for Cu^{2+} was slightly reduced in the presence of 2.5 meq/l. Ca^{2+} falls within the error ($\pm 10\%$) inherent in the x-ray analysis.[10] Taking this error into account, both Cu^{2+} curves are essentially the same. Neither of these columns ever broke through; that is, all of the copper ion was removed from solution by the substrate.

The two TPS columns run with Pb^{2+} as the heavy metal ion (Fig. 7) show almost the same results as those of Figure 6, with all of the Pb^{2+} taken out by the 25th cm of the column. Analytical error again accounts for differences between the two Pb^{2+} curves up to about the 15th cm. Beyond this point Pb^{2+} sorption is slightly higher in the presence of Ca^{2+}, which was indicated in batch results (Fig. 1). In both cases (copper and lead), Ca^{2+} was sorbed minimally until a

decrease in the heavy metal concentration on the packing allowed more Ca^{2+} to be taken up. Again this tends to show competition for sorption sites between the light and heavy metal ions.

Due to the similarity of WAB and RMB batch test results, only WAB was used in column experiments. Two runs were made with WAB as the substrate, first with a control solution of 0.5 meq/l. Zn^{2+} and second with a feed solution of 0.5 meq/l. Zn^{2+} and 2.5 meq/l. Ca^{2+}. The results are shown in Figure 8. As in the batch experiments, Zn^{2+} uptake was only slightly reduced by the presence of Ca^{2+} in the feed solution. However, it was found that white ash bark itself contains a high concentration of Ca^{2+} (1.5–1.75 meq/g). Except for the first few substrate sections, the concentration of Ca^{2+} on the WAB packing was essentially the same whether the feed solution contained Ca^{2+} or not. With the control solution (no added Ca^{2+}), the Ca^{2+} naturally occurring in WAB was displaced by Zn^{2+} in the first few column sections but resorbed farther up the column length. When Ca^{2+} was present in the feed solution, displacement of Ca^{2+} by Zn^{2+} on the substrate was reduced, and the first few sections had a higher Ca^{2+} concentration.

In the Zn^{2+} (0.5 meq/l.) control column (Fig. 8), most of the Zn^{2+} was sorbed near the column inlet, while Zn^{2+} uptake in the presence of added Ca^{2+} (2.5 meq/l.) was more constant over the entire length of the column, indicating a slightly negative effect of Ca^{2+} on the uptake of Zn^{2+}.

CONCLUSIONS

In choosing a substrate for removal of heavy metal ions from a waste stream, several factors must be considered: the species of heavy metal to be removed, the concentration of light metal ions in the stream, and substrate characteristics. Various substrates have differing affinities for different heavy metals ions, and various light metal ions can interfere to a greater or lesser extent in the binding of the heavy metal ions.

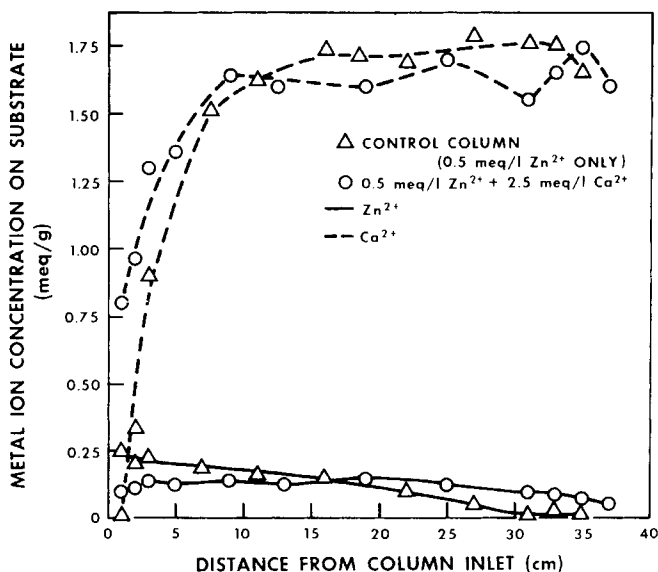Formaldehyde-treated peanut skins are an excellent substrate for the removal

Fig. 8. Distribution of Zn^{2+} and Ca^{2+} on WAB substrate in packed-column tests.

of Pb^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+} from solution. However, relatively high concentrations of light metals (especially Ca^{2+}) can reduce the effectiveness of the TPS sorption of Cd^{2+} and Zn^{2+}.

White ash and So. Wisconsin red maple barks are also effective in heavy metal ion removal and, in the case of Cd^{2+} and Zn^{2+}, would be preferable to TPS as a substrate. The high concentration of naturally occurring Ca^{2+} in WAB does not inhibit sorption of the heavy metals tested.

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