Removal of Cupric Ion from Solution by Contact with Peanut Skins

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Synopsis

Certain tannin-containing agricultural wastes, such as peanut skin, are highly efficient ion exchange materials for the removal of cupric ion from aqueous waste solutions. Concentrations of Cu^{2+} as high as 200–1000 ppm can be reduced to less than 0.5 ppm by pouring the waste solution through a short column of peanut skin. The column packing can take up greater than 10% of its weight in copper, even from 50 ppm solution. Complete regeneration of the packing is readily achieved by eluting the Cu^{2+} from the column with $0.1N$ HCl. The ion exchange process is pH dependent, with optimum removal of copper from solution occurring in the 5–7 pH range. Two hydrogen ions are liberated into solution for each Cu^{2+} attached to the peanut skin, so pH decreases as reaction continues, inhibiting the reaction. Thus, a continuous column process would be more efficient than a stepwise batch process.

INTRODUCTION

The presence of heavy metal ions in our waters has generated considerable concern in recent years. Mercury pollution has received the greatest share of attention, and strict Federal and Local waste water standards have been set up or proposed. The removal of mercuric ion from polluted waters by contact with agricultural wastes has been reported by Friedman and Waiss.[1]

However, mercury is not the only heavy metal cation which is deleterious to plant and animal life. Cupric ion is an important contaminant in some waste waters. Seepage of cupric ion from old copper mines can eliminate all fish and plants from streams for miles downstream from the source.[2]

A number of methods have been proposed and are being used to remove copper from industrial waste solutions. A recent review[3] discusses many of these methods and systems for a number of heavy metals. Basic precipitation of Cu^{2+} from solution is often used industrially to reduce Cu^{2+} concentration in waste waters. Ion exchange can be quite efficient in removing copper from solution,[4] but synthetic ion exchange resins are expensive. Few of the methods currently being used to remove heavy metals from industrial wastes can consistently meet the recent strict water quality standards. A process which can consistently reduce copper below 0.5 ppm in effluent is urgently required.

Various natural products such as clays and wood bark can remove heavy metal cations from streams. A somewhat similar natural product is peanut skin,

a waste agricultural product from the roasting and packing of Virginia peanuts. Like bark, peanut skins and other nut wastes are high in tannin components. Cupric ion forms chelates with catechol,[5] which is much like tannin in that it is a ring compound with multiple adjacent hydroxyl groups. It is suspected that tannin may form similar chelates with cupric ion. Peanut skin is virtually worthless, does not decompose rapidly in contact with water, and adsorbs fairly large amounts of copper. This report will examine the sorption of cupric ion by peanut skin and insolubilized peanut skin.

EXPERIMENTAL

Adsorbent

Two forms of peanut skin were used. One was untreated peanut skin, and the other was peanut skin which was treated with acid and formaldehyde to polymerize and insolubilize tannins.

Fresh untreated peanut skin was washed with an excess of water, air dried to approximately 20% moisture at room temperature, and ground to pass through the 1-mm screen of a Wiley mill. The adsorbent was ground in order to increase surface area and to reduce wall effects in small packed columns.

Untreated peanut skin has the disadvantage that some color (and thus BOD) is leached by water, which turns a reddish color. Much of this soluble color is low molecular weight tannin compounds. In order to prevent the leaching of color into solution and the loss of potentially useful tannins, fresh peanut skin was treated to fix the leachable colors and form the material called "ground formaldehyde treated peanut skin," or GFTPS: 1 kg of unwashed skin was mixed with 10 liters of $0.2N$ H_2SO_4 and 500 g of 35% formaldehyde. The mixture was stirred well and allowed to stand for 2 hr at about 50°C. Upon separation of skins from residual liquid, the liquid was clear. The HCHO polymerized and insolubilized the colored, water-soluble tannins in place, for there was no fine precipitate or curd which would indicate that the tannins were extracted into solution and then polymerized. The product was air dried and ground as above.

Sections of 20-mm-i.d. glass pipe were used for packed columns. Adsorbent was placed dry into the column. The column was tapped very gently to promote even distribution of packing in the column. 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 through the column, 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.

Equilibrium experiments were carried out by combining 1.0 g peanut skin with 100 ml solution in a 250-ml glass-stoppered Erlenmeyer flask. The mixture was gently agitated for at least 1 hr to ensure equilibrium and then filtered. The solid was dried at 40°C to approximately 4% moisture.

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.[6] In this nondestructive technique, a wafer

TABLE I
Comparison Between Washed Peanut Skin (GWPS) and Formaldehyde-Treated Peanut
Skin (GFTPS) in Adsorption of Cu^{2+} from Solution

Concn of Cu^{2+} in feed, ppm	Concn of Cu^{2+} in aqueous effluent, ppm	
	GWPS	GFTPS
10	0.2–0.3	0.22
50	0.4–0.5	0.4–0.55
85	1.0	2.8

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 Giauque et al.[7]

Analysis—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

Adsorbents

Table I compares the adsorption efficiencies of ground washed peanut skin and ground formaldehyde-treated peanut skin in taking up and holding cupric ion. The formaldehyde-treated material was nearly as efficient as the nontreated material. Furthermore, the handling characteristics of the formaldehyde-treated material were better. The washed peanut skins were soft and tended to disintegrate in water, producing very fine particles which were difficult to filter. However, the formaldehyde-treated peanut skins were quite friable and easily ground and showed no signs of disintegration even when immersed in water for long periods.

The superior handling characteristics of the GFTPS appeared sufficient to make the slight cost of formaldehyde treatment worthwhile. Washing peanut skins free of color required many liters of water per kilogram of skin. Treatment with formaldehyde fixed the color and produced relatively small quantities of liquid waste which could be reused. It was expected that GFTPS would be more stable than washed peanut skin in acid regeneration media. Because of these numerous advantages, GFTPS was used in all further experiments.

Adsorption Rates

Tests with cupric ion indicated that Cu^{2+} reaction rates were similar to previous results for Hg^{2+}, where adsorption of Hg^{2+} reached approximately 70–80% of the equilibrium value in 1 min and 90% or more in 5 min, almost independent of
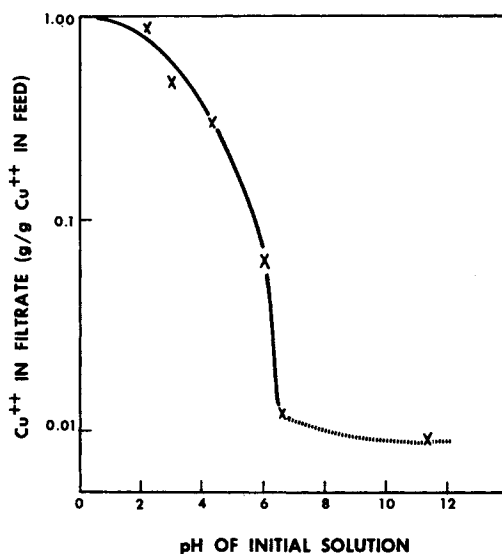
Fig. 1. Effect of pH on the removal of Cu^{2+} from cupric acetate solution.

initial Hg^{2+} concentrations from 10–100 ppm. Thus, for Cu^{2+} it was assumed that a contact time of 30 min or more was adequate for equilibrium conditions to be reached.

Effect of pH

For an equilibrium test Figure 1 shows that the efficiency of adsorption of Cu^{2+} on peanut skin was a function of pH of the initial solution. Above a pH of 6.8, $Cu(OH)_2$ precipitated; the point at pH 11.3 was obtained by complexing the copper with added ammonia for solubility. Maximum adsorption appeared to be obtained at pH 6 and above. Little or no adsorption occurred below a pH of about 2.5.

Adsorption Isotherms

Efficiencies of adsorption of Cu^{2+} from several dilute aqueous solutions of copper compounds and from a mixture of equal concentrations of Cu^{2+}, Pb^{2+}, and Hg^{2+} acetates were measured. These adsorption isotherms for $Cu(OAc)_2$, for $CuCl_2$, and for Cu^{2+} from the Cu, Pb, Hg acetate mixture are shown in Figure 2. The isotherm for $CuSO_4$ was determined but was virtually the same as that for $CuCl_2$. Both Figure 2 and Table II show greater adsorption of Cu^{2+} from $Cu(OAc)_2$ solution than from $CuSO_4$ or $CuCl_2$ solution. The isotherm for the mixture of Cu, Pb, and Hg acetate shows somewhat less equilibrium adsorption of Cu^{2+} from the mixture than from a pure $Cu(OAc)_2$ solution. This is quite understandable if it is assumed that Pb and Hg compete with copper for available sites, inhibiting the removal of Cu^{2+} from solution.

It was hypothesized that ion exchange is the principal mechanism of copper removal. It has been known for many years that cupric ion is readily taken up by Amberlite synthetic ion exchange resins.[4] Thus, it is quite possible that the same mechanism controls with peanut skin. From the nature of the materials which are efficient in capturing heavy metal ions, it can be speculated that tannins
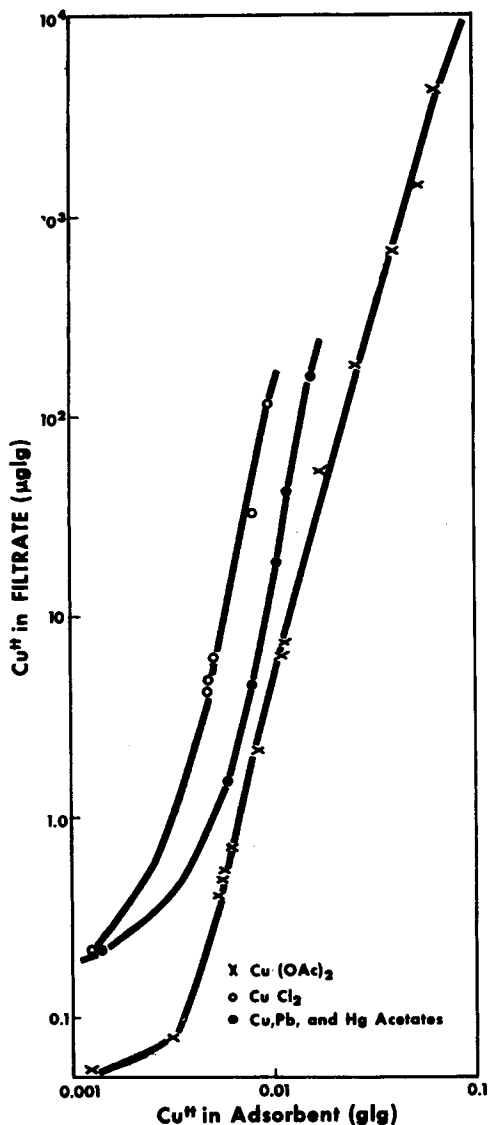
Fig. 2. Adsorption isotherms for several copper solutions.

are the active ion exchange compounds and that the active sites are the phenolic groups of the tannin. A cupric ion could attach itself to two adjacent hydroxyl groups, releasing two hydrogen ions into solution.

The equilibrium was quite dependent upon pH. Each of the feed solutions of cupric acetate, chloride, and sulfate was approximately the same concentration and pH, and yet removal of Cu^{2+} was more complete from acetate solution than from the other solutions (Fig. 1). In each case, the pH of the filtered effluent was less than that of the feed solution, but the pH of effluents from acetate solutions were much higher than from chlorides or sulfates, as can be seen in Table II. The acetate had a buffering effect on the solution which limited the lowering of pH and allowed the removal of Cu^{2+} to proceed, unhindered by dependence

TABLE II

Effect of Anion on the Equilibrium Removal of Cu^{2+} from 100 ml of
Aqueous Solution by 1.0 g GFTPS[a]

Copper salt		Added salt		Cu^{2+} in effluent	pH	
Anion	Feed concn	Compound	Concn		Feed	Effluent
Acetate	50			0.42	5.95	5.60
Acetate	50	NaCl	10	0.4	5.95	5.60
Acetate	50	NaCl	50	0.5	5.95	5.62
Chloride	50			4.7	5.90	3.25
Sulfate	50			4.3	5.85	3.35
Acetate	85			2.8	6.17	3.96
Acetate	85	NaCl	100	3.5	6.17	4.12
Chloride	95			33.	5.83	2.94
Chloride	95	NaOAc	100	1.	5.80	4.79
Sulfate	95			32.	5.71	3.00
Acetate	500			220.	5.94	4.56
Acetate	500	NaOAc	1000	180.	5.94	4.84
Chloride	500			450.	5.14	2.77
Chloride	500	NaOAc	1000	340.	5.14	4.10

[a] All Cu^{2+} concentrations in parts per million.

upon the Cu^{2+}–H^+ equilibrium. Assuming that ion exchange is the principal mechanism, the equilibrium should be quite dependent on pH, and the results bear this out. In most cases, removal of Cu^{2+} from solution ceased as the pH of the solution in contact with the adsorbent dropped to 3.5–4.5. When the pH was further lowered by the removal of Cu^{2+} solution and the introduction of $0.1N$ HCl, the equilibrium was reversed. Cupric ion was stripped from the solid into the acid. The peanut skin, which had turned dark brown as it captured cupric ion, turned orange again as Cu^{2+} was stripped from the adsorbent. The HCl solution became dark blue, with Cu^{2+} concentrations as high as 1%.

As a verification of the hypothesis that cupric ion attaches itself to two hydroxyl groups, releasing two hydrogen ions into solution, the theoretical pH change of a $CuCl_2$ solution was calculated from the experimentally verified change in Cu^{2+} concentration as adsorption occurred. Experimentally, 50 mg Cu^{2+} disappeared from 1 liter of solution. Hypothetically, this would produce 57.5 mg HCl/l., with a pH of approximately 2.82. The actual pH of the final solution was 2.77, in good agreement with the calculated value.

Nonequilibrium Tests

In actual field operation of the process, it is likely that a packed column would be used to adsorb metal ions. A continuous process employing 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 maintained. If the liquid flow rate is slow, the process approximates equilibrium from point to point in the column.

Several aqueous cupric acetate solutions with Cu^{2+} concentrations ranging from 50 to 1000 ppm were treated by passing them through packed beds of peanut skin. In all cases, Cu^{2+} was reduced to less than 0.1 ppm until the bed began to overload. The results are shown in Table III.

TABLE III
Removal of Cu^{2+} from Acetate Solution in a Packed Bed[a]

	Concentration of Cu^{2+} in feed, ppm					
			200[b]			
	50	50	I	R	S	1000
Flow rate, bed volumes/hr	0.31	2.4	1.0	0.5	1.0	2.4
Total feed, g Cu^{2+}/g adsorbent	0.011	0.0490	0.042	—	0.038	0.046
Feed at steady state conditions, g/g	0.011	>0.035	0.039	—	0.036	0.020
Steady state concn, ppm Cu^{2+}	<0.050	<0.050	<0.050	3300[c]	<0.050	<0.010
Final effluent concn, ppm Cu^{2+}	<0.050	22	21.0	550	0.22	540
Total Cu^{2+} adsorbed or eluted, g	—	0.985	—	0.802	—	—
Copper adsorbed at top of column, g/g	0.0515	0.0960	—	—	0.1042	0.0846
Copper adsorbed at bottom of column, g/g	0.000023	0.0266	—	—	0.0000702	0.0347

[a] Packing was 25 g of GFTPS, 45 mm in height, in a 20-mm-i.d. glass column.

[b] I = Initial adsorption experiment; R = regeneration step; S = second adsorption experiment.

[c] Eluted with 350 ml of 0.1N HCl.

Two examples are shown for a 50-ppm Cu^{2+} feed. The first example gives the results for a packed column with excess capacity, while the second represents a column which has just begun to overload. Concentration of Cu^{2+} on the adsorbent at the bottom of the column was quite low at the conclusion of the run with the unsaturated column, indicating that the 45-cm packing height provided sufficient contact time for Cu^{2+} takeup.

In all the other runs, sufficient Cu^{2+} was introduced to overload the column, so that the concentration of Cu^{2+} in the effluent eventually rose above 0.1 ppm. This was done to determine the capacity of the column for feeds of different Cu concentrations. The capacity of a peanut skin column, in g Cu^{2+} fed/g adsorbent, was about the same for 50–200-ppm feeds but was substantially lower for a 1000-ppm feed. The different capacities can be explained by noting that in a packed column there is an adsorption zone of finite length over which most of the ion removal occurs. As the adsorbent becomes saturated, the zone moves slowly down the column until it reaches the bottom, at which point the concentration of metal ion in the effluent starts to increase. A high-concentration feed solution requires a longer adsorption zone to reach a desired effluent concentration than a low-concentration feed solution. Since the columns used were relatively short compared to the length of the adsorption zone for the 1000-ppm feed, the zone for this concentrated feed reached the bottom of the column before much of the adsorbent in the upper part of the column became saturated with Cu^{2+}. If the column were made as long relative to the length of the adsorption zone as for lower-concentration feeds, the capacity would be as great or greater.

In each of the packed column experiments, the pH of the effluent followed the same pattern. The pH of the feed was usually about 6. At steady-state conditions, the effluent pH was usually in the range of 3.6–3.8. Only when Cu^{2+} began to increase in the effluent did the pH also begin to rise. Thus, there was at least a qualitative correlation between pH and Cu concentration. So long as the pH of the effluent was constant at 3.6–3.8, steady state obtained and there was no problem. The first sign of a definite increase in pH was an indication that the column had begun to overload. The point at which feeding of waste would cease and regeneration of the column would begin could be automatically controlled by monitoring the pH of the effluent from the bed. This could be a valuable quality control tool in operation of a packed bed.

The fact that removal of Cu^{2+} from solution is reversible and greatly dependent upon pH can help explain the discrepancies between data in Figure 2 and Table III. The amount of Cu^{2+} in the adsorbent at the top of the packing in each packed column experiment in Table III was several times as great as would be expected from an examination of the adsorption isotherms in Figure 2 (using the feed Cu^{2+} concentration as the ordinate). However, the data of Figure 2 were obtained under equilibrium conditions, in which the pH of the effluent solution was always less than the pH of the feed and ultimately was determined by the amount of Cu^{2+} taken up by the adsorbent. In the packed column, the situation was quite different. The adsorbent was in contact with a solution of fixed concentration *and* of fixed pH. Under these conditions, where pH had no effect, takeup of Cu^{2+} could continue until all available sites for attachment of copper were used up. The situation is roughly equivalent to a small amount of adsorbent placed in contact with a nearly infinite amount of solvent.

Regeneration of Packing

A packed column of GFTPS was contacted with $Cu(OAc)_2$ solution (200 ppm Cu^{2+}), stripped with $0.1N$ HCl, washed, and then contacted again with 200 ppm Cu^{2+}. The results are given in Table III. In the column representing 200 ppm Cu^{2+} feed, I was the original feed, R the regeneration step, and S the final feed. The results of I and S runs were quite similar. The amount of copper taken up under steady-state conditions and the steady-state Cu^{2+} concentrations in the effluents were approximately the same for both runs. The packing was thus about as active in taking up copper after it was regenerated as it had been when fresh. There was no apparent physical breakdown of the packing. Upon regeneration, it appeared almost the same as it had when new.

The $0.1N$ HCl used to elute the Cu^{2+} from the packing easily flowed through the column without leaving unreacted spots, as was evidenced by the dramatic change in color of the packing from brownish black back to the orange of new packing. The pH of the effluent (pH of acid eluant was 1.2) was about 3.5 at the beginning, rose to 4.5–5.0 at maximum Cu^{2+} in the effluent (3300 ppm), and then rapidly dropped to 1.2–1.3 as the copper concentration decreased.

Treatment of Mine Water

A sample of runoff water (pH 6.33) from an abandoned copper mine was obtained. Seepage from this mine is sufficiently toxic to destroy fish and vegetation in a nearby stream. The cupric ion concentration was 6.0 ppm, probably lower

than normal because of recent rains. No difficulty was encountered in reducing the Cu^{2+} content below 0.1 ppm by contact with peanut skin.

CONCLUSIONS

Peanut skin, treated or untreated, is an excellent substrate for the removal of cupric ion from aqueous solution, dilute or concentrated. The concentration of Cu^{2+} can be easily reduced below the maximum levels in waste water prescribed by local or federal governmental agencies. Few of the methods now commonly employed to reduce Cu^{2+} in waste water can effectively reduce the concentration below 0.5 ppm. Treatment with peanut skin or other agricultural waste affords a promising method for meeting proposed water quality standards.

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