Removal of Trace Quantities of Nickel From Solution

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Synopsis

Chitosan, which is produced from the natural polymer chitin, is a much more efficient scavenger of nickel ion than other natural ion exchange materials tested. An industrial waste containing about 7 ppm Ni^{2+} and 10,000 ppm Na^{+} was reduced to less than 0.1 ppm Ni^{2+} by contact in a packed column of chitosan. Capacity of the chitosan substrate under these conditions was a little more than 1 meq/g. The substrate can be regenerated by contact with buffered NH_4Cl at pH 10. The high sodium content of the nickel waste did not prevent sorption of Ni^{2+}, but it apparently produced an interference with atomic absorption spectrophotometer analyses, giving a spurious reading of 0.8 ppm Ni^{2+} when the major nickel line at 232 nm was used for analysis.

INTRODUCTION

Research has been carried out on removal of toxic heavy metal ions from liquid waste streams by contact with various natural products, including peat moss,[1] bark,[2–5] nut wastes,[6,7] sawdust,[8] starch derivatives,[9] cotton,[10] wool,[11,12] sewage sludges,[4,13] and others.[4] In general, much of the work has been concentrated on removing the most toxic heavy metal ions, such as Hg^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+}. These four heavy metals are among the most easily removed from solution. Almost all of the natural polymers can remove one or more, or even all, of these four ions quantitatively, often with high substrate capacity.

For example, redwood bark can reduce Cu^{2+} to less than 0.05 ppm, with a capacity of up to 10% Cu by weight on the bark.[14] Results are quite similar for the other metal ions mentioned.[2] However, little work has been done on another important contaminant, nickel, which is prevalent in wastes from metal plating and chemical industries. Most of the previous research was either not concerned with scavenging to a very low residual level or had indicated that even when scavenging was almost complete, the capacities of the natural substrates for Ni^{2+} were low, limiting the practical use of the process.

These limitations on the treatment of nickel wastes led us to search for a natural polymer which would meet the following criteria: (a) remove nickel quantitatively, (b) have sufficient capacity for the metal to make waste treatment economically feasible, and (c) be easily regenerable. Previous preliminary studies[4,15] indicated that chitosan, the deacetylated product of the natural polymer chitin, might be able to satisfy these criteria. In this report we demonstrate the use of chitosan in packed columns to scavenge nickel ion from dilute industrial nickel waste.

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Experimental

Chitosan was obtained from Food Chemical Company, Seattle, Washington. It is produced commercially by deacetylation of chitin (from shrimp or lobster shells) with sodium hydroxide at high temperature. Other samples were prepared in the laboratory by a similar method. For use in small columns, chitosan was ground in a Wiley mill to pass a 20-mesh screen.

Dried, ground formaldehyde-treated peanut skin was prepared in the laboratory by treating fresh peanut skin with formaldehyde under acidic conditions.[6]

Samples of nickel waste solution were obtained from a nickel chemical manufacturing company and were used as is for various experiments. Other nickel test solutions of various concentrations were prepared by dissolving reagent-grade $Ni(NO_3)_2 \cdot 6H_2O$ or $NiCl_2 \cdot 6H_2O$ in distilled water.

Sections of 9-mm glass pipe were used for columns. Chitosan was slurried with water, poured into the column, and allowed to settle. Peanut skin was packed dry into the column and then wetted by flow of water through the column. Glass beads were added on top of the packing to prevent adsorbent particles from floating and to prevent the packing from separating.

Flow of test solutions through the column was upward, by hydrostatic head, controlled by stopcocks at top and bottom of the column. Effluent from the column was sampled intermittently for metal analysis. At the conclusion of a run, the column was washed with a few bed volumes of water and drained. The packing was sectioned into 1- or 2-cm increments and dried in an oven at 60°C for 24 hr. The sectioned column packing samples were analyzed for metal content by x-ray fluorescence spectrometry.

Nickel analyses of solid samples were carried out with a Quanta/Metrix Model 70 energy-dispersive x-ray fluorescence spectrometer (Finnegan Corp., Sunnyvale, California) by a method similar to that described by Giauque and Jaklevic.[16] In this nondestructive technique, a wafer of material is subjected to a beam of rhodium x-rays, and the characteristic fluorescent x-rays are detected and stored as a function of energy and intensity.[13]

Liquid samples were analyzed for nickel with a Perkin-Elmer 303 atomic absorption spectrophometer, using the major line for nickel (232.0 nm). Qualitative analyses for nickel ion were carried out with the nickel–dimethylglyoxime standard test.

RESULTS AND DISCUSSION

The divalent metal ion Ni^{2+} is not bound to nearly the extent of lead or copper on most natural ion exchange materials. Although formaldehyde-treated peanut skin can bind lead up to 20% by weight[7] and copper better than 10% by weight,[6] the capacity for binding Ni^{2+} is much lower, as can be seen in Table I. The peanut skin column removed Ni^{2+} quite well for a short time, as evidenced by the steady-state concentration of less than 0.1 ppm Ni^{2+} in the effluent from the column. However, the sorption capacity of the packaging was low, with Ni^{2+} appearing in the column effluent after only a little over 50 mg Ni^{2+} had been fed to the column. Overall, the peanut skin substrate bound only 0.114 meq Ni^{2+}/g substrate before the column broke through, as compared to 0.464 meq/g for Pb^{2+} and 0.635 meq/g for Cu^{2+} under similar conditions.[6,7] Uptake results similar to those with peanut skin were obtained with redwood bark.[2]

TABLE I
Removal of Ni^{2+} from $NiCl_2$ Solution in a Packed Bed of Ground, Formaldehyde-Treated Peanut Skin[a]

Ni^{2+} concentration in feed, ppm	21.0
Flow rate, bed volumes/hr	3.5
Total feed, liters	7.6
Feed at steady-state conditions, liters	2.5
Total Ni^{2+} sorbed at steady state, meq/g	0.144
Steady state Ni^{2+} concentration in effluent, ppm	<0.1
pH of feed	7.58
pH of steady-state effluent	3.42

[a] Packing was 16 g peanut skin packed to a depth of 24 cm in a 25-mm-I.D. glass column.

It had been found in equilibrium studies with high concentration of metal salts that chitosan picked up much more nickel from solution than did some other natural products.[4] On this basis it seemed likely that chitosan might be better than peanut skin or bark for scavenging small quantities of Ni^{2+} from dilute solutions. A liquid waste product from manufacture of nickel compounds was obtained. The waste contained 7.5 ppm Ni^{2+} by atomic absorption (AA) analysis. A small packed column of chitosan was set up and nickel waste run through it. The results are given in Table II. Analysis of the effluent from the column after about 5 liters of solution was passed through showed that the column never did break through, that is, the concentration of nickel ion in the effluent remained constant throughout the run. However, the concentration of Ni^{2+} in the effluent was analyzed by AA and found to be 0.8 ppm (shown in the "Apparent value" column of Table II). This concentration was higher than expected.

The sorption profile of the chitosan substrate from the above column is shown in Figure 1. It is apparent that for the dilute nickel waste, the maximum binding capacity of Ni^{2+} by chitosan was approximately 30 mg Ni^{2+} per gram chitosan. The nickel bound on the substrate at the column exit was approximately 0.1 mg/g; it is probable that the column would have broken through if much more nickel waste had been fed to the column. The shape of the binding curve for nickel on chitosan was similar to those for other heavy metals on natural substrates[15] and, although the maximum capacity of 1 meq/g was lower than for copper, lead, or cadmium on some other substrates in similar column tests, it would appear to be adequate for application.

TABLE II
Removal of Nickel from Industrial Waste Solution in Packed Bed of Chitosan[a]

	Apparent values	Corrected values
Ni^{2+} concentration in feed, ppm	7.5	6.7
Flow rate, bed volumes/hr	15–17	15–17
Total feed, liters	5.0	5.0
Feed at steady-state conditions, liters	5.0	5.0
Steady-state Ni^{2+} concentration in effuent, ppm	0.8	< 0.1
pH of feed	8.74	8.74
pH of effluent	8.8–9.0	8.8–9.0
Total Ni^{2+} removed from solution, mg	33.4	33.4
Nickel on substrate at column entrance, mg/g	29.2	29.2
Nickel on substrate at column exit, mg/g	0.104	0.104
Total nickel on column, mg	32.8	32.8

[a] Packing was 3.0 g chitosan, packed to a depth of 15 cm in a 9-mm-I.D. glass column.

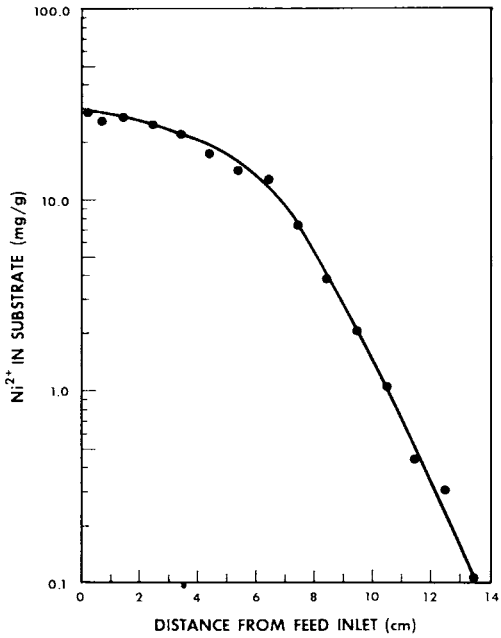

Fig. 1. Ni^{2+} sorption profile of chitosan-packed bed.

The atomic absorption value of 0.8 ppm Ni^{2+} remaining in solution in the effluent from the chitosan column seemed high. Although this level was lower than the 1.0 ppm allowable limit for nickel often encountered, it seemed quite high when compared to 0.1 ppm obtained, albeit for a short time, from experiments described in Table I for removal of Ni^{2+} from nickel salt solutions by polymerized peanut skins. Efforts to further treat the effluent to reduce the 0.8 ppm value failed. These included running the effluent from the chitosan column through a fresh chitosan column or through a peanut skin column. The nickel reading remained 0.8 ppm, raising a question of whether this level may have been an artifact. The treated effluent was tested for nickel ion by a qualitative test with dimethylglyoxime. A solution known to contain 0.8 ppm Ni^{2+} [from $Ni(NO_3)_2$] showed the typical pink precipitate, indicating that the test was sensitive at this low level. However, the nickel waste effluent from the chitosan column showed no pink precipitate at all. If nickel was present, it was not in the form of Ni^{2+}.

Analysis of the nickel waste had shown that it contained an unusually high sodium concentration, about 10,000 ppm. When solutions of 10,000 ppm Na^+ from reagent-grade NaCl, Na_2SO_4, or $NaNO_3$ were analyzed by AA with the nickel hollow cathode lamp at the same wavelength (232.0 nm) used to analyze the column effluents for nickel, a peak appeared which was the same height as the peak obtained from treated nickel waste. Apparently, the 0.8 ppm reading for nickel was caused by sodium (or a common contaminant in sodium salts), an interference which has apparently not been reported in atomic absorption literature. This interference was experienced on the Perkin-Elmer Model 303 spectrophotometer, which has no light baffles. Analysis on newer instruments may not be affected in the same manner or degree.

The chitosan column had actually reduced Ni^{2+} in the waste below the atomic absorption detection limits for nickel (0.1 ppm), and the corrected Ni^{2+} con-

centration of the original waste solution was 6.7 ppm instead of 7.5 ppm. These corrected nickel concentrations are shown in the last column of Table II.

If the use of chitosan as a scavenger of heavy metal ions is to be economical, the chitosan must be regenerable, to reuse the valuable substrate and to produce a concentrated nickel solution from which the nickel can be easily separated. Nickel can be stripped from chitosan substrate with weak bases. Ammonium hydroxide partially eluted nickel from chitosan, but buffered NH_4Cl solutions stripped nickel more completely. Batch tests on chitosan saturated with nickel showed that good regeneration was obtained by contacting the substrate with 0.1–0.2*N* NH_4Cl brought to pH 10 with NH_4OH. Results of two of these tests are shown in Table III.

In run 1, chitosan was contacted with 0.1*N* NH_4Cl at pH 9. Removal of nickel was incomplete, so the liquid was drained and discarded. The same substrate was then contacted with two 30-ml volumes of 0.2*N* NH_4Cl at pH 10. In run 2, the substrate sample was contacted with two 30-ml volumes of 0.1*N* NH_4Cl at pH 10. Regeneration was fairly good with both 0.1 and 0.2*N* NH_4Cl (95% and 97% nickel removal, respectively), as long as the pH of the eluant was about 10. Perhaps three contacts with 0.2*N* NH_4Cl were responsible for the slightly higher degree of regeneration compared to two contacts with 0.1*N* NH_4Cl. In regeneration of a packed column, fresh eluant continually contacts the substrate, and regeneration would be more complete than for either of the batch tests. Furthermore, more concentrated eluates could be obtained, allowing easier recovery of nickel by precipitation, or other means.

Conclusions

Of a number of natural heavy metal scavengers which have been tested, only chitosan displayed sufficient binding capacity to be potentially important for cleaning up industrial nickel wastes. Chitosan has a different binding mechanism than the other materials tested, most of which act as acid-form ion exchangers. The mechanism by which metal ions are bound by chitosan probably involves attachment of these ions to —NH_2 groups in the chitosan. Because

TABLE III
Regeneration of Chitosan Substrate with Buffered NH_4Cl Solution

	Run 1	Run 2
Substrate used, g	0.6	0.6
Ni^{2+} on saturated substrate, mg/g	47.9	47.9
Eluant 1	0.1*N* NH_4Cl	0.1*N* NH_4Cl
Ni^{2+} in eluate 1		
pH	9	10
ppm	140	880
Eluant 2	0.2*N* NH_4Cl	0.1*N* NH_4Cl
Ni^{2+} in eluate 2		
pH	10	10
ppm	745	76
Eluant 3	0.2*N* NH_4Cl	
Ni^{2+} in eluate 3		
pH	10	
ppm	34	
Ni^{2+} on regenerated substrate, mg/g	0.56	2.40
Regeneration, %	97	95

of its different mechanism, chitosan may be suitable for scavenging important heavy metal ions and complexes that cannot be adequately treated by other natural polymers. These include Cr^{3+}, copper–cyanide complex, silver-containing photographic wastes, and others.

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

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