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The Isolation of Cobalt, Nickel, and Copper from Manganese Nodules by Chelation Chromatography on Chitosan

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Abstract

The separation of cobalt, nickel, and copper from manganese and iron is performed on chitosan columns in the presence of a reducing agent, preferably sulfite or ascorbic acid. The procedure is applied to recover valuable metals from manganese nodules after solubilization with sodium hydrogen sulfate at 215°C.

Chitosan, a chelating polymer of marine origin derived from chitin, has been of great help in the recent past to provide new analytical chromatographic methods for the determination of copper, molybdenum, and vanadium in seawater (*1–5*).

Furthermore, the chelating ability of chitosan for a number of ions has been demonstrated to increase in sulfuric acid + ammonium sulfate solutions, while remaining negligible for manganese, and very low for ferrous ions (*6*). This information about chitosan qualifies this polymer as a very attractive chromatographic support for the separation of cobalt, nickel, and copper from manganese and iron (*7*, *8*).

Today, the isolation of valuable metals from manganese nodules is very important because marine ores mainly composed of manganese and iron oxides and containing up to 2.7% of cobalt, nickel, and copper, in addition to several other elements, await exploitation for the industrial production of the latter three metals.

The metals in the manganese nodules are mainly in the form of oxides and occur in a peculiar physical form. The physicochemical structure of the manganese nodules is a result of the conditions to which they have been exposed since their formation. Marine nodules have never been exposed to temperatures higher than those of the deep ocean waters. They have an extremely large surface area and often better than 50% porosity, thus they are a reactive ore.

The matrix of marine nodules is a complex crystal matrix of manganese and iron oxides which holds other metal oxides, the most important being cobalt, nickel, and copper in addition to vanadium, chromium, and several others (*9*). A certain amount of silt or gangue is intimately admixed in the nodules; it includes oxides of silicon and aluminum. The precise chemical composition of the nodules depends on the location from which they come. Explorations are being conducted especially in the Pacific and Indian Oceans. Oceanographic ships supply data on chemical and mineralogical characteristics of the nodules for a computerized mapping of these resources on a worldwide basis (*10–12*). Common techniques used to refine land ores are not generally suitable for the nodules. Technology has struggled with various schemes for refining manganese nodules, mainly based on dissolution in hydrochloric acid and subsequent ion-exchange separation. Chloridation has been mentioned as a possibility; this includes reaction with sodium or calcium chloride at 1100°C. Chlorides can then be separated by sweeping the chlorides formed with a stream of nitrogen; chlorine and reducing agents have also been used (*13*). A molten mixture of nodules and chlorides was kept at 1000°C for several hours and volatile chlorides removed and condensed in a jet spray containing hydrochloric acid. Solvent extraction with 8-quinolinol or other complexing agents was then performed. Other works included ion exchange (*14*, *15*).

It is clear, therefore, that there is still a place for further improvement or for new approaches to the isolation of valuable metals from manganese + iron matrices. This paper, based on the chelating ability of chitosan and its peculiar behavior toward manganese and ferrous ions in sulfate solutions, is offered as a contribution to the advancement of the marine nodule technology as well as an interesting example of chelation chromatography.

EXPERIMENTAL

Solubilization of Marine Nodules

The solubilization of manganese nodules has been carried out in sodium hydrogen sulfate or in potassium hydrogen sulfate. The temperature required for fusion is around 215°C; the manganese nodules are soluble in molten salt due to the chemical attack by sulfuric anhydride originated in the decomposition of the salt. The resulting mass is soluble in water and yields a clear solution.

The solubilization has also been performed with sodium carbonate at 850°C. At this temperature, oxygen from air oxidizes manganese to manganate and the resulting mass is therefore green.

The dissolution in dilute acids decomposes the carbonate and yields permanganate and manganese dioxide. The mixture of concentrated sulfuric acid and 30 volumes of hydrogen peroxide is also suitable for the dissolution of manganese ores.

Of course, for the purpose of this investigation, the first dissolution procedure has been preferred because it requires low temperature and a commonly available salt, and yields clear solutions of manganese in the lowest oxidation state. This procedure also provides sulfate anions as the reaction product, which favors subsequent chromatographic separation. Acidic dissolution has been adopted for the analytical purposes only.

Instrumentation

A Perkin-Elmer 305 atomic absorption spectrometer equipped with both flame atomizer and PE-70 graphite atomizer, deuterium background compensation, and strip-chart recorder was used. To simulate manganese + iron ores, the following solution was prepared and was used to establish the chromatographic conditions: Mn 52.6%, Fe 31.6%, Co 5.2%, Ni 5.2%, and Cu 5.2%. Sulfates were preferred for this purpose. To this solution sodium or potassium sulfate was added, when desired, to simulate experimental conditions including melting in sodium or potassium hydrogen sulfate.

Aliquots of this solution were mixed with the required chemical and percolated through chitosan columns (250 mg, 15 × 8 mm or 200 mg, 60 × 5 mm) at a flow rate of 20 ml/min. The chitosan powder was previously conditioned with 30 ml of 0.1 *M* sulfuric acid + ammonium sulfate, washed with water (20 ml), with 1 *M* ammonia (10 ml), and with water to the desired pH value. Manganese was determined in the effluents while Fe, Co, Ni, and Cu were determined in the elution fractions obtained after passing the 0.1 *M* sulfuric acid + ammonium sulfate mixture which ensures the total elution of the metals examined. The conditions adopted with the 15 × 8 mm columns were such as to give preliminary data only (Figs. 1 to 7) useful to establish the most suitable conditions for chromatographic separations.

RESULTS AND DISCUSSION

Reduction

It is known that chitosan does not appreciably collect manganous and ferrous ions. Therefore, the reduction of ferric to ferrous ion was investigated in order to ensure the elution of most if not all the iron, with no alteration of the collection of the other metal ions; the reductive complexation of iron for the same purpose was also investigated as a possible way to improve the separation. It should be noted that iron is present in manganese nodules in varying amounts, sensibly lower than manganese. Thus the separation of iron is needed especially in those cases where its concentration is not negligible.

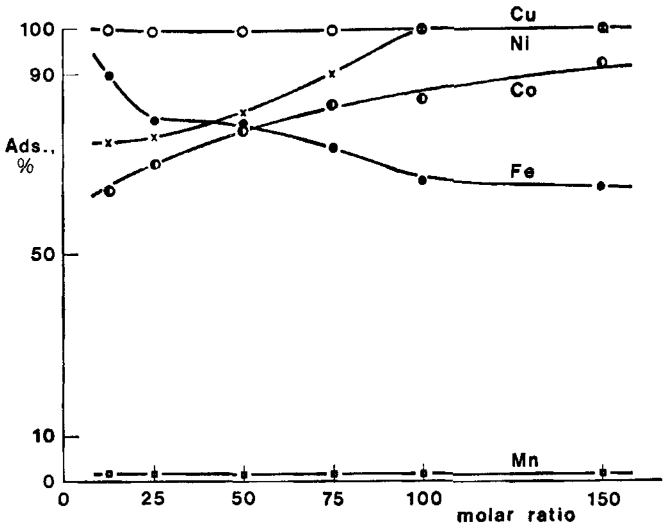

FIG. 1. Percent of adsorption of metal ions in the reciprocal presence on chitosan as a function of the molar ratio sulfite/iron. pH, 7.0; sulfate concentration, 30 m*M*; column, 15 × 8 mm; flow rate, 20 ml × min^{-1}.

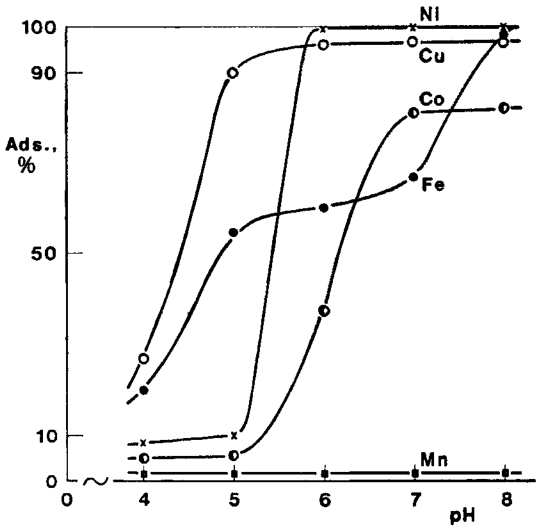

FIG. 2. Percent of adsorption of metal ions in the reciprocal presence on chitosan as a function of pH. Sulfate concentration, 30 m*M*; sulfite concentration, 6.2 m*M*; column, 15 × 8 mm; flow rate, 20 ml × $\min^{-1}$.

The metal ion solution (1 ml) at pH 7.0, containing 0.2 g/l of sodium sulfate with added amounts of sodium sulfite (final volume 50 ml), was percolated through the preconditioned chitosan column. Figure 1 shows the adsorption percent for the five metals in reciprocal presence as a function of the molar ratio sulfite/iron. Sulfite lowers the adsorption percent of iron while a better adsorption percent can be obtained for nickel and cobalt. The copper and manganese curves are not affected by the increasing concentration of sulfite ion.

Under constant conditions the pH variation indicates the best separation condition at pH 7.0 (Fig. 2), where the complete adsorption of copper and nickel is accompanied by a good yield of cobalt. The retention of iron into the chitosan column is still rather high.

Complexation

The same conditions indicated above have been adopted for studying the effect of oxalic acid on chromatographic separation. Figure 3 shows the adsorption percent of the five metals as a function of the molar ratio oxalate/iron. A general trend is the depression of the adsorption for all of the ions collected, especially for iron and cobalt.

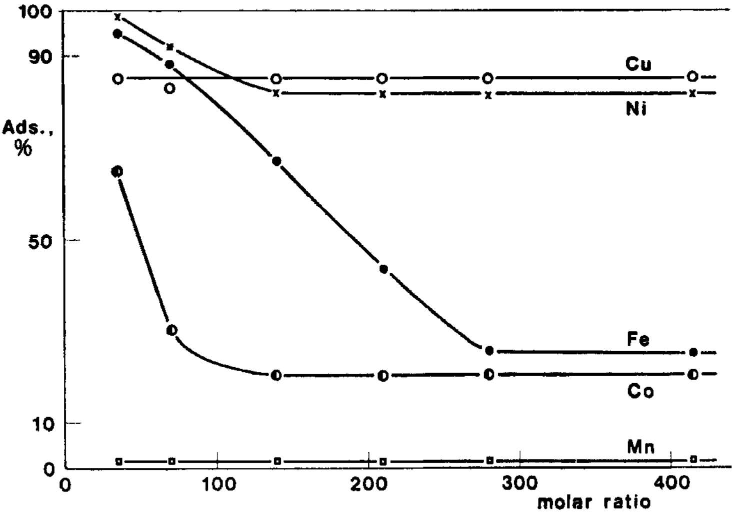

FIG. 3. Percent of adsorption of metal ions in the reciprocal presence on chitosan as a function of the molar ratio oxalate/iron. pH, 7.0; sulfate concentration, 30 m*M*; column, 15 × 8 mm; flow rate, 20 ml × min^{-1}.

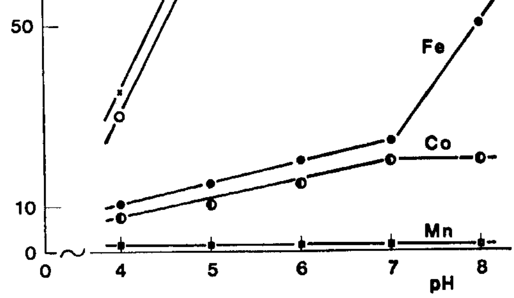

FIG. 4. Percent of adsorption of metal ions in the reciprocal presence on chitosan as a function of pH. Sulfate concentration, 30 m*M*; oxalate concentration, 6.2 m*M*; column, 15 × 8 mm; flow rate, 20 ml × min^{-1}.

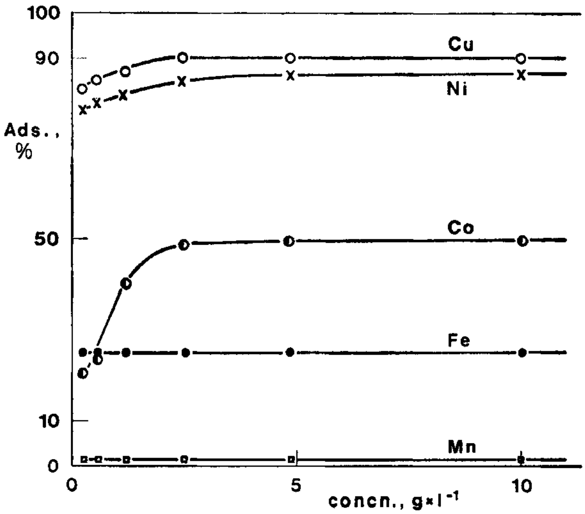

FIG. 5. Percent of adsorption of metal ions in the reciprocal presence on chitosan as a function of the sulfate concentration at the best conditions evidenced in Figs. 3 and 4. pH, 7.0; molar ratio, oxalate/iron = 300; column, 15 × 8 mm; flow rate, 20 ml × min^{-1}.

Under standard conditions, with a ratio oxalate/iron = 300, the pH variation makes the adsorption of cobalt increase slightly, but does not substantially represent a way of improving the chromatographic performance (Fig. 4).

A certain effect of the sulfate concentration has been demonstrated at pH 7.0 and a molar ratio oxalate/iron = 300, as shown in Fig. 5. The cobalt adsorption rises to about 50%, while iron and manganese keep their low values. This means that the variations in the amounts of sodium hydrogen sulfate used to dissolve the ore or varying compositions of the same do not alter the general results of the chromatographic procedure.

Reductive Complexation

Ascorbic acid has been tested under the above-mentioned conditions as a reducing and complexing agent for its effect on minimizing the interaction of chitosan with ferrous ion. Figure 6 shows that ascorbic acid dramatically lowers the retention of ferrous ion on chitosan columns while permitting copper and nickel to be totally adsorbed and cobalt to be adsorbed at about 80%. Manganese is not adsorbed at all. At the

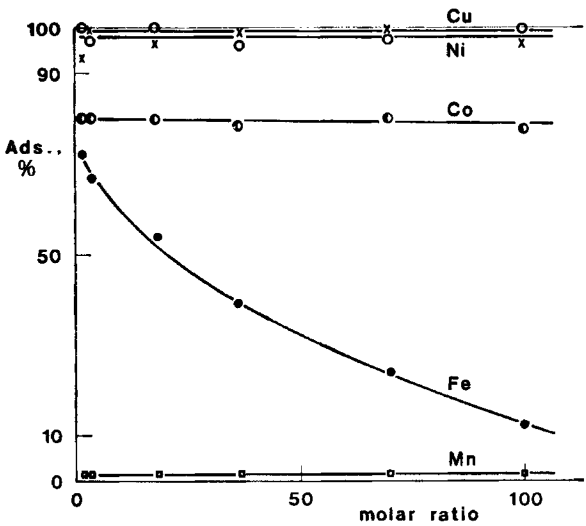

FIG. 6. Percent of adsorption of metal ions in the reciprocal presence on chitosan as a function of the molar ratio ascorbic acid/iron. pH, 7.0; sulfate concentration, 30 mM; column, 15 × 8 mm; flow rate, 20 ml × min^{-1}.

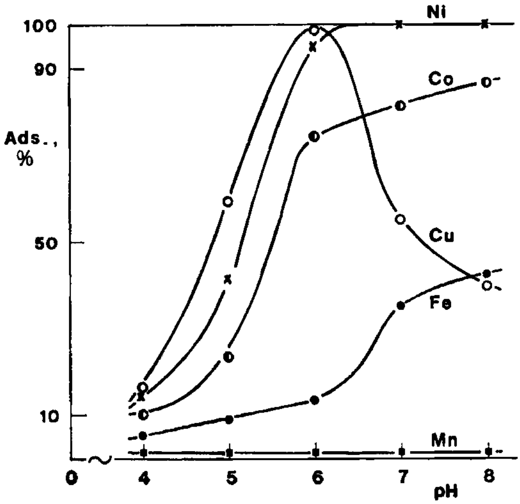

FIG. 7. Percent of adsorption of metal ions in the reciprocal presence on chitosan as a function of pH. Sulfate concentration, 30 mM; ascorbic acid present; column, 15 × 8 mm; flow rate, 20 ml × min^{-1}.

molar ratio ascorbic acid/iron = 100, 88 % of iron passes through the column together with 100 % manganese and about 20 % cobalt.

The presence of ascorbic acid prevents metal ions from precipitating in the form of hydroxides even at elevated pH values because of its complexing action; however, chitosan chelates cobalt, nickel, and copper even when they are brought into its presence as ascorbic acid complexes. As shown in Fig. 7, particularly favorable conditions are met at pH 6.0. At this pH value a good separation of manganese and iron from cobalt, nickel, and copper has been made.

Column Regeneration

Chitosan columns have been recycled 20 times according to the following sequence: (1) metal ion solution (1 ml) at pH 6.0 with added ascorbic acid in the ratio ascorbic acid/iron = 100 and sodium sulfate (4 g/l), final volume 50 ml; (2) water (20 ml) to wash out excess disodium sulfate; (3) 0.1 *M* sulfuric acid + ammonium sulfate mixture to perform elution; (4) water (20 ml); (5) 1 *M* ammonia (10 ml); and, finally, (6) water to reach pH 6.0. The columns did not lose their chelating ability as the results of the 20th cycle are similar to those of the first.

The saturation of a column of 200 mg chitosan 60 × 5 mm gave breakthrough curves as follows for the immediate saturation with iron and manganese. After 50 ml of solution, corresponding to 33 free column volumes, the retention of cobalt was about 70 % while the retention of nickel and copper was total. After 100 ml (66 free column volumes), the retention of cobalt was 48 % while the retention of nickel was 78 % and of copper was still 100 %. The absolute amounts involved were 1.5 mg of each metal. The same was verified with nodules whose composition was Mn 18 %, Fe 0.54 %, Cu 0.15 %, and Ni 0.10 %. These data indicate that the operating conditions for the chromatographic recovery of the valuable metals should take into account the tendency of cobalt to partially escape from the column, and therefore the best conditions should be those which represent a compromise between a partial loss of cobalt and the extended saturation of the column with nickel and copper before recycling.

CONCLUSIONS

The use of chitosan columns conditioned in sulfuric acid and ammonium sulfate has been demonstrated to be of great help in performing the rapid separation of cobalt, nickel, and copper from manganese solutions obtained after dissolution of marine nodules in sodium or potassium hydrogen sulfate. When it is desired to perform simultaneously a separation from manganese and iron, the addition of reducing agents permits avoidance of the retention of ferric ions on chitosan; when the nodules contain a low proportion of iron, the use of reducing agents may be omitted.

The proposed method requires little thermal energy for carrying out the fusion, relies on the use of commonly available chemicals, and yields the metals of interest as a dilute sulfuric acid solution which is suitable for electroplating or stripping. Chitosan is a commercially available, low-priced polymer which can be regenerated and recycled many times.

Acknowledgments

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