

Comparison Study of Copper Ion Adsorption on Chitosan, Dowex A-1, and Zerolit 225

W. S. WAN NGAH, I. M. ISA

School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

Received 3 February 1997; accepted 6 June 1997

ABSTRACT: The adsorption of copper ions by chitosan, Dowex A-1, and Zerolit 225 has been investigated. The uptake of copper was determined from changes in concentration as measured by atomic absorption spectrometry. A preliminary investigation on the adsorption was conducted by batch-wise examining the effects on pH and the initial copper ion concentration. It was found that chitosan has an excellent loading capacity of copper, compared with Dowex A-1 and Zerolit 225. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1067–1070, 1998

Key words: comparison study; copper ion; adsorption; chitosan; Dowex A-1; Zerolit 225

INTRODUCTION

The use of direct determination atomic absorption spectrometry or other analytical techniques for trace metal analysis sometimes has always been plagued by several problems due to matrix effects, contaminations, loss of constituents, and other problems. Several separation or preconcentration techniques have been used to achieve good sensitivity, accuracy, and reliability before determination can be made. Brooks and colleagues¹ have shown that a number of trace elements in saline waters can be separated by extraction of their complexes with ammonium pyrrolidine dithiocarbamate into methyl isobutyl ketone and subsequent analysis by atomic absorption spectrometry. The chemistry underlying the behavior and use of the commercial chelating ion exchange resin for collection of trace metal is reasonably well understood.^{2–4} The analytical application of the chelating ion exchange resin has become in-

creasingly popular, compared with other techniques. The chelating ion exchange resins are easy to use, less time-consuming, and allow much higher concentration factors to be attained. Florence and Batley² have used a column of Chelex-100 chelating resin for the retention of copper, lead, cadmium, and zinc from sea water, and analyzing the original and column effluent using direct anodic stripping voltammetry.

Chitosan, a poly(D-glucosamine), is prepared from chitin by deacetylating its acetoamide groups with a strong alkali solution. Chitin is a natural polymer extracted from crustacean shells, such as prawns, crabs, insects and shrimps. Chitosan has already been described as a suitable natural polymer for the collection of metal ions^{5–15} through chelation, due to the presence of an amino group of the 2-amino-2-deoxy-D-glucose (glucosamine) unit. Although a considerable number of articles have so far been published concerning the adsorption of metal ions on chitosan, there have been only a few articles concerning the comparison adsorption behavior between chitosan and commercial chelating polymers. The objective of this study was to study the adsorption of copper by chitosan, Dowex A-1,

Correspondence to: W. S. Wan Ngah.

Journal of Applied Polymer Science, Vol. 67, 1067–1070 (1998)
© 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/061067-04

and Zerolit 225 as a function of concentration using atomic absorption spectrometry.

EXPERIMENTAL

Reagents and Apparatus

All of the reagents used were of analytical reagent grade. Doubly distilled water was used to prepare all the solutions. Stock solutions of copper were prepared by using copper sulfate salt. Samples of chitosan prepared from the shells of prawns were kindly donated from Chitin-Chitosan Research Centre (Universiti Kebangsaan Malaysia). Chitosan was used in the form of 100–200 mesh powder. Two different commercial resins were used in this investigation:

1. Dowex A-1 (Bio-Rad Laboratories, Richmond, CA), 100–200 mesh, supplied in the chloride form. To convert the resin into the H^+ -form, 20.0 g of Dowex A-1 was suspended in 100 mL of 1M hydrochloric acid, followed by suspension in 100 mL of 1M nitric acid. The resin was then washed with distilled water until the pH of the effluent was about pH 7.
2. Zerolit 225 (BDH Chemical Ltd., Poole, Dorset, UK), 14–52 mesh, supplied in the $-SO_3H^+$ -form. To convert the resin into the H^+ -form, the same procedure as Dowex A-1 was followed by using 10.0 g of Zerolit 225.

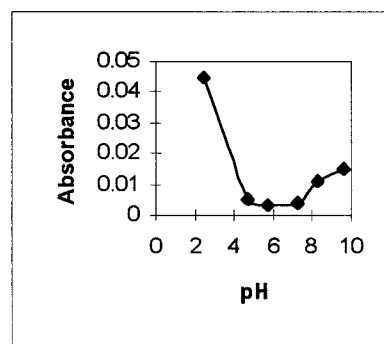
The resins were packed into 12-mm diameter glass tubes. A GBC model 903 atomic absorption/ flame emission spectrophotometer (Victoria, Australia) was used for the analysis.

pH Dependence of Copper Complexation

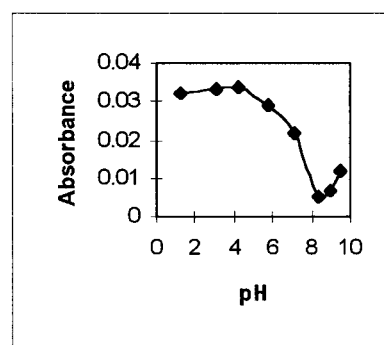
Stock solutions containing 100.0 ppm copper ion were prepared over a range of pH. Ten-milliliter aliquots were passed through a 0.2 g chitosan column. The column tap was adjusted to give a flow rate of 1.0 mL/min. The chitosan column had earlier been washed with distilled water. The effluent was collected in a 100 mL volumetric flask. Columns were then washed with distilled water, and the combined effluents were made up to 100 mL with distilled water. The absorbances of the resin effluent solution were determined using the

atomic absorption spectrophotometer. For copper ion adsorption on Dowex A-1, stock solutions containing 10.0 ppm copper ion were prepared over a range of pH. Ten-milliliter aliquots were passed through a 20.0 g Dowex A-1 column. For copper

(a) Chitosan



(b) Dowex A-1



(c) Zerolit 225

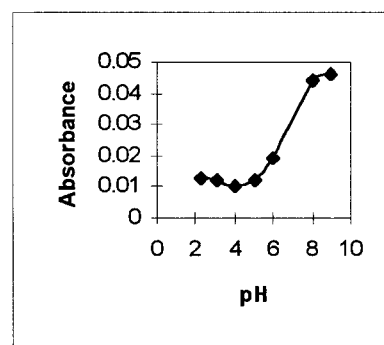


Figure 1 The effect of pH on chitosan, Dowex A-1, and Zerolit 225 adsorption.

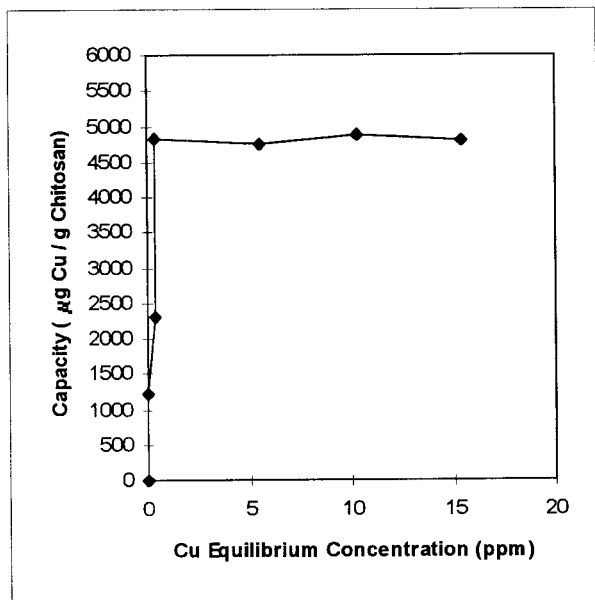


Figure 2 Adsorption of copper (Cu) on chitosan.

ion adsorption on Zerolit 225, stock solutions containing 100.0 ppm of copper ions were prepared over a range of pH. Fifty-milliliter aliquots were passed through a 10.0 g Zerolit 225 column. The same procedure as chitosan was followed.

Determination of Resin Capacity

The capacity of the copper ion adsorption was determined for chitosan, Dowex A-1, and Zerolit 225. Stock copper ion solutions containing 10.0 ppm at pH 6.2 for determination of chitosan capacity, 100.0 ppm at pH 8.6 for determination of the Dowex A-1 capacity, and 100.0 ppm at pH 4.1 for determination of the Zerolit 225 capacity were prepared. Different volumes of the stock solutions were introduced into the different resin columns, and the effluents were collected in the 100-mL volumetric flask. Columns were washed with distilled water. The amount of copper remaining in the combined effluent was determined using the atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

The effect of pH on the adsorption of copper ion using chitosan, Dowex A-1, and Zerolit 225 are shown in Figure 1. The pattern found in these figures showed that the resins can only be used

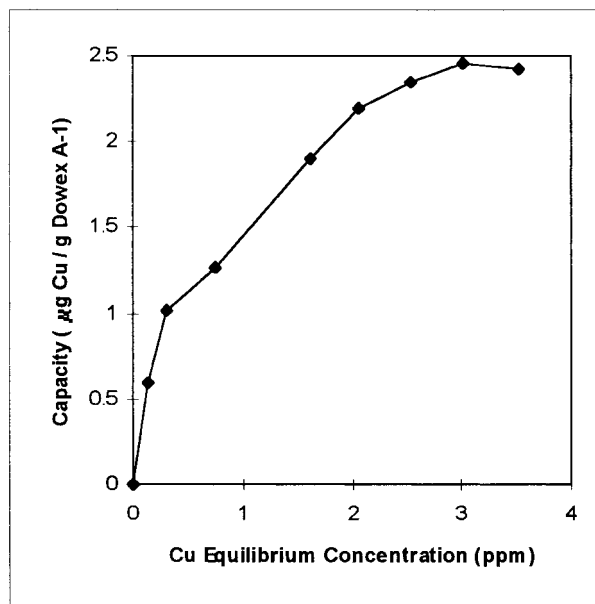


Figure 3 Adsorption of copper (Cu) on Dowex A-1.

for the uptake of copper ion over a restricted range of pH values. The pH of the copper ion solutions was found to have a significant effect on the degree of metal complexation or adsorption by the chelating resin used. Copper could only be chelated quantitatively at pH 6.2 for chitosan, at pH 8.6 for Dowex A-1, and at pH 4.1 for Zerolit 225.

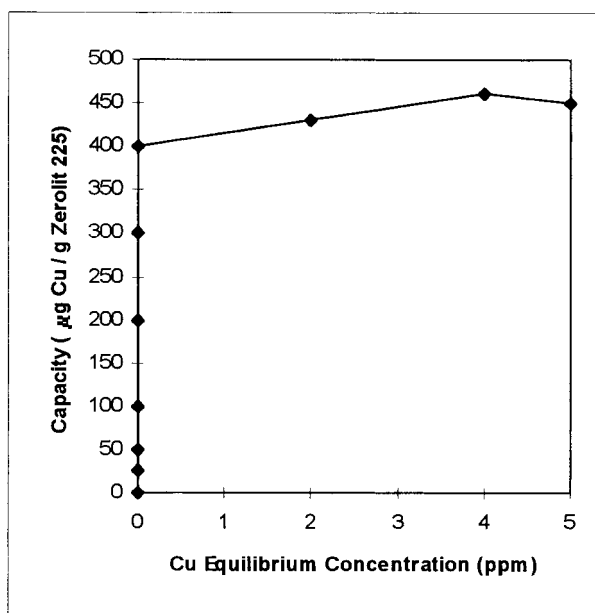


Figure 4 Adsorption of copper (Cu) on Zerolit 225.

Table I Limiting Adsorption of Copper (Cu) by Chitosan, Dowex A-1, and Zerolit 225

Resin	Capacity ($\mu\text{g Cu/g resin}$)
Chitosan	4700
Dowex A-1	2.3
Zerolit 225	440

The adsorption capacity of resin has been calculated from the equation:

Resin capacity

$$= \frac{(\text{initial amount of Cu} - \text{final amount of Cu})}{\text{amount of resin used}}$$

The results for the adsorption capacity of the resin for copper ions are shown in Figures 2–4. It can be seen that the adsorption capacity increases as the concentration of copper ion increases until an equilibrium concentration is reached. The numerical data for the maximum adsorption capacity of the resin used are summarized in Table I. The result clearly demonstrates that chitosan has a greater specific adsorption capacity than that of the commercial chelating resin used. The greater adsorption capacity by chitosan, compared with Dowex A-1 and Zerolit 225, may be due to the amino groups in chitosan that are much better ligands for binding to copper ions, compared with the iminodiacetic acid groups in Dowex A-1 and the sulfonic acid groups in Zerolit 225. The amino group on each anhydroglucose ring of the chitosan chain serves as chelation sites for copper ions, because there are more available electrons on the nitrogen atom.

Adsorption of the copper ions is accompanied by the appearance of a deep blue color. The significant conclusion herein is that the adsorption of copper on Dowex A-1 is only $\sim 0.05\%$ and on Zerolit 225 is only $\sim 9.4\%$ of that on chitosan. Chitosan columns are very effective in collecting copper. Inoue and colleagues¹² explained that the excellent adsorption behavior of chitosan for metal ion is due to: (1) the high hydrophilicity of chitosan with a large number of hydroxyl groups; (2) the large number of primary amino groups content with high activity; and (3) the flexible structure of the polymer chains of chitosan, which enables a suitable configuration for complexation with metals ions.

CONCLUSIONS

The results obtained confirm that chitosan in the powder form can collect copper ion because the polymer chelates the copper ions. Chitosan is a very useful chelating agent, compared with a commercial one. The technique based on the column of chitosan for collection of copper ions from solution is proposed as a useful analytical tool. We believe that chitosan should find wide applications in the treatment of waste waters, trace metal pre-concentration, or recovery of trace metals.

We are indebted to Chitin-Chitosan Research Centre, Universiti Kebangsaan Malaysia (Selangor, Malaysia) for supplying samples of chitosan.

REFERENCES

1. R. R. Brooks, B. J. Presley, and I. R. Kaplan, *Talanta*, **14**, 809 (1967).
2. T. M. Florence and G. E. Batley, *Talanta*, **23**, 179 (1976).
3. J. P. Riley and D. Taylor, *Anal. Chim. Acta*, **40**, 479 (1968).
4. M. I. Abdullah, O. A. El-Rayis, and J. P. Riley, *Anal. Chim. Acta*, **84**, 363 (1976).
5. R. A. A. Muzzarelli, *Chitin*, Pergamon Press, Oxford, 1976.
6. R. A. A. Muzzarelli, *Natural Chelating Polymers*, Pergamon Press, Oxford, 1973.
7. C. Kantipuly, S. Katragadda, A. Chow, and H. D. Gesser, *Talanta*, **37**, 491 (1990).
8. M. S. Masri and V. G. Randall, in *Proceedings of the First International Conference on Chitin / Chitosan*, R. A. A. Muzzarelli and E. R. Pariser, Eds., MIT Sea Grant Program, Cambridge, 1978, p. 277.
9. R. Maruca, B. J. Suder, and J. P. Wightman, *J. Appl. Polym. Sci.*, **27**, 4827 (1982).
10. G. McKay, H. S. Blair, and A. Hindon, *Indian J. Chem.*, **28A**, 356 (1989).
11. C. A. Eiden, C. A. Jewell, and J. P. Wightman, *J. Appl. Polym. Sci.*, **25**, 1587 (1980).
12. K. Inoue, Y. Baba, and K. Yoshizuka, *Bull. Chem. Soc. Jpn.*, **66**, 2915 (1993).
13. K. Ohga, Y. Kuauchi, and H. Yanase, *Bull. Chem. Soc. Jpn.*, **60**, 444 (1987).
14. C. Peniche-Covas, L. W. Alvarez, and W. Arguelles-Monal, *J. Appl. Polym. Sci.*, **46**, 1147 (1992).
15. W. S. W. Ngah, M. J. Jais, A. Alimuniar, and Z. A. Haharap, in *Chitin and Chitosan, The Versatile Environmentally Friendly Modern Material*, M. B. Zakaria, Ed., UKM, Malaysia, 1995, p. 275.