Separation Science and Technology

ISSN: 0149-6395 (Print) 1520-5754 (Online) Journal homepage: http://www.tandfonline.com/loi/lsst20

Application of Chitosan Membranes in Separation of Heavy Metal Ions

Władysław Kamiński & Zofia Modrzejewska

SEPARATION SCIENCE AND TECHNOLOGY, 32(16), pp. 2659–2668, 1997

Application of Chitosan Membranes in Separation of Heavy Metal Ions

WŁADYSŁAW KAMIŃSKI and ZOFIA MODRZEJEWSKA
FACULTY OF PROCESS AND ENVIRONMENTAL ENGINEERING
TECHNICAL UNIVERSITY OF ŁÓDŹ
UL. WÓLCZAŃSKA 175, 90–924 ŁÓDŹ, POLAND

ABSTRACT

The authors present an application of chitosan membranes for the removal of heavy metal ions. Investigations covered membranes produced by phase inversion. Additionally, separation properties of acetylated membranes were tested. Low-viscous chitosan produced by the Sea Fisheries Institute—Poland was used in the experiments. The investigations were carried out for the transition metal ions Cr(VI), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II). A method for metal ions separation by means of chitosan membranes was proposed. The metal ions were complexed in the membrane during ultrafiltration of the solution. The separation ability of the membranes was investigated for individual metal ions and for a mixture. The effect of the pH of the solution on separation properties of membranes was determined. The concentration of metal ions was investigated by the method of inductively coupled plasma (ICP) atomic emission spectrometry. The investigations show the suitability of chitosan membranes produced by the phase inversion method for the removal of metal ions.

Key Words. Membrane preparation and structure; Acetylated membranes; Ion separation selectivity

INTRODUCTION

Recently, an intensive development of studies on polymers which bind metal ions has been observed. Studies on the polymer–metal complexes are of great practical importance. Complexing abilities of polymers are used in chromatographic methods for the selective separation of metal ions in nuclear chemistry, electrochemistry, hydrometallurgy, and environmental protection.

The complexing properties of chitosan have been known for a long time. They are caused by an advantageous location of —OH and —NH_2 groups in the molecule (1). Chitosan salts or powdered chitosan are usually used in chelation because of their expanded contact area. Chitosan balls are also used as active absorbents.

It is well known that chitosan forms chelate compounds with metal ions with a release of hydrogen ions (2–6). Hence, the adsorption of metal ions on chitosan depends strongly on the pH of the solution being tested. An example of the formation of chitosan chelates with copper ions is shown in Fig. 1.

Of particular significance among many methods of metal ions separation is the one which combines two processes: complexing of a polymer with metal ions and ultrafiltration of the complexes through membranes of proper selectivity (7).

In this paper a method for metal ions separation by means of chitosan ultrafiltration membranes is proposed. Measurements were carried out for a single metal ion and for ion combinations. Solutions with pH ranging from 3.0 to 11 were tested. The effect of acetylation on separation properties was determined and is discussed.

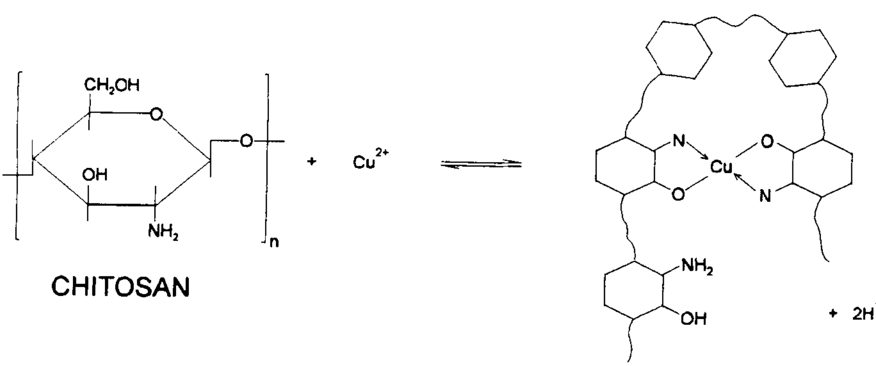

FIG. 1 Formation of chitosan chelates with copper ions.

EXPERIMENTAL

Materials and Method

The tests were carried out on the basis of two types of low-viscous chitosan: 57 and 69 produced by the Sea Fisheries Institute in Gdynia, Poland, with the parameters listed in Table 1.

The average molecular weight was determined by the viscometric method (8), the degree of deacetylation by a method described in the Polish Standards (9), the water retention value by a method described previously (10), the crystallinity index by the x-ray method and the viscosity with the use of a Brookfield viscometer by the method described in the Polish Standards (9).

Preparation of Chitosan Membranes

The membranes were produced by the phase inversion methods with a 7% chitosan solution in 2% acetic acid. The solution was poured onto a flat surface. A proper membrane thickness was formed by using an applicator with a 0.8-mm slot. Immediately after the solution was poured, the process of coagulation was carried out in a 4% aqueous solution of sodium hydroxide for 15 minutes. After washing with tap water, the membranes were conditioned in demineralized water for 4 hours and then washed with demineralized water for 30 to 40 minutes to obtain pH 7.5.

Preparation of Acetylated Membranes

Membranes were acetylated under the conditions given by Yaku and Yamashita (1), i.e., in the bath containing 100 parts of methanol, 3 parts of acetic anhydride (97%), and 3 parts of dehydrating agent (*N*,*N*′-dicyclohexylcarbodiimide) at 25°C for 1 hour.

TABLE 1
Parameters of Chitosans 57 and 69

	Chitosan 57	Chitosan 69
Average molecular weight	2.05×10^5 D	3.01×10^5 D
Deacetylation degree	78.44%	78.89%
Crystallinity index	64%	67%
Water retention value	137.4%	178%
Viscosity	0.057 Pa·s	0.069 Pa·s
Nitrogen	7.2%	7.4%

Method for Metal Ions Separation

Metal ions were separated by chitosan membranes using the ultrafiltration method. The membrane thickness and process parameters were selected to allow metal ions to be complexed in the membrane. The ultrafiltration process was carried out at room temperature (20–23°C). Separation abilities of the membranes were tested in the pressure range from 0.05 to 0.2 MPa (with increments of 0.05 MPa). In the investigations, 200 mL of output solution was used. During ultrafiltration, 10 mL of permeate was collected at every pressure level.

Separation abilities of membranes were tested by determining the retentivity of ions by the membrane during ultrafiltration. Investigations were carried out for the metal ions Cr(VI), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II). Solutions for experiments were made from standardized nitric acid solutions. Demineralized water was used for dissolution. Solutions with pHs ranging from 3.0 to 11 were prepared.

A quantitative determination of elements was made by inductively coupled plasma (ICP) atomic emission spectrometry using Perkin-Elmer Plasma 400 equipment.

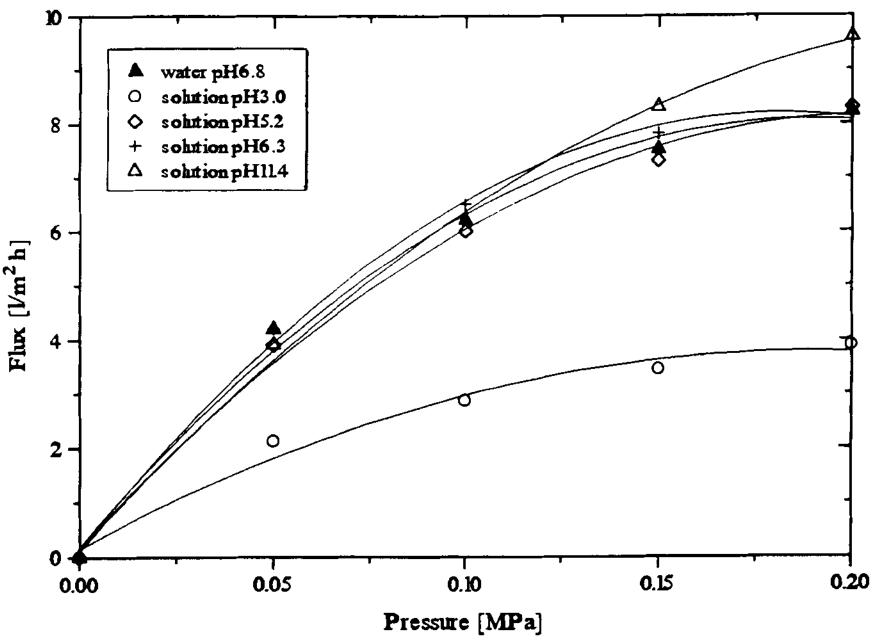

FIG. 2 Ultrafiltration of metal ions solutions at different pH values (chitosan 57).

DISCUSSION

The Effect of pH on Separation Properties of Membranes

Abilities of ion removal of metals which were a mixture of many components [Cr(VI), Zn(II), Cd(II), Ni(II), Co(II), Fe(III), Mn(II), and Cu(II)] were tested for a chitosan membrane made from two different low-viscous chitosans. The permeation flux was determined according to pressure for pure solvent (demineralized water) and solutions containing metal ions. Solutions with the pH ranging from 3 to 11 were analyzed. Results are shown in Figs. 2 and 3 for chitosans 69 and 57, respectively.

Although these chitosans come from the same group (low viscosity chitosans), they are different, which undoubtedly affects their separation abilities.

Chitosan 57 membranes are characterized by a higher permeation flux both for water and the solutions being tested. The higher permeation flux for chitosan 57 membranes is probably due to its lower weight-average molecular weight. Film-generating solutions made from chitosan 57 are characterized by a lower viscosity which causes the membranes produced

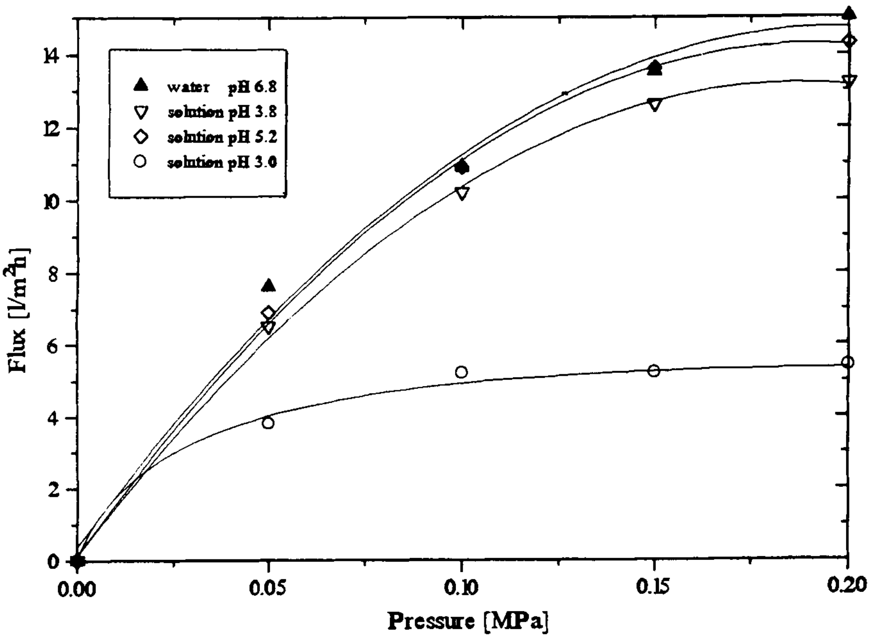

FIG. 3 Ultrafiltration of metal ions solutions at different pH values (chitosan 69).

from them to have a looser structure. The looser structure, in turn, makes the time of contact of the solution and membrane shorter, and hence the separation ability may be reduced.

Additionally, chitosan 69 has a higher WRV index which proves that its inner structure is more developed, its absorptivity and water-holding capacity are higher, and stronger hydrogen bonds can be formed as a result.

For membranes produced from both chitosans 57 and 69 it was found that for ultrafiltration of solutions at pH 3 there was a significant reduction in permeation flux, while for solutions of pH 3.6 to 11 the permeation flux was close to that obtained for demineralized water of pH 6.8. However, most of the ions are separated by the membranes over a wide range. The ions of Cu(II), Cd(II), Ni(II), Co(II), and Zn(II) are separated almost completely by the membranes in the 3 to 5.6 pH range. The content of ions in the permeate does not exceed 6%.

Separation of Fe(III) ions was investigated at pH 3 [Fe(III) ions are precipitated at a higher pH]. The absorbance of Fe(III) ions by the membrane is shown because they are not present in the permeate and their

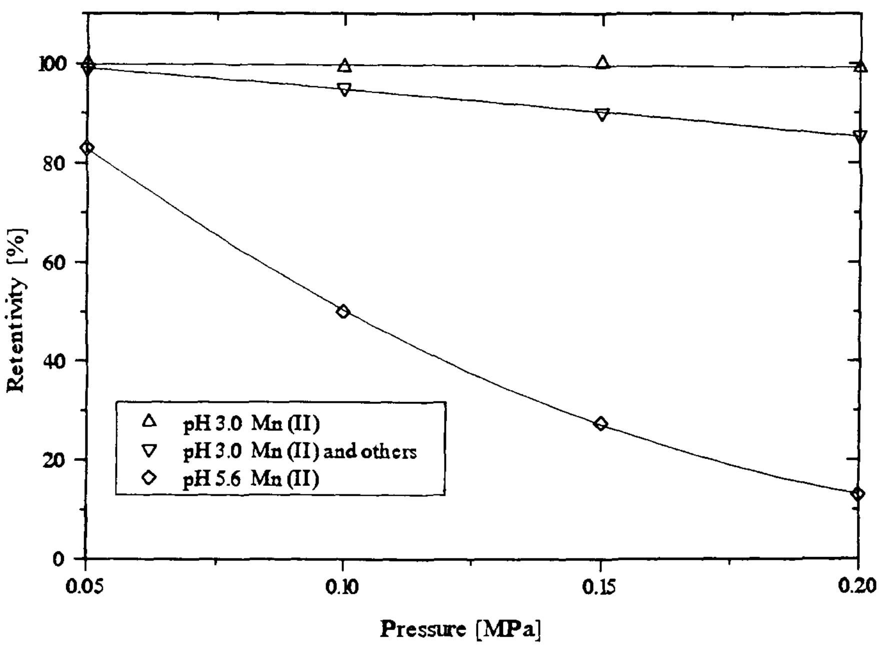

FIG. 4 Mn(II) ion separation on the chitosan membrane (chitosan 57).

concentration in the retentate decreases. For example, after 68 minutes of ultrafiltration during which the solution is in contact with the membrane, the concentration of ions in the initial solution is reduced by 21%.

The separation properties of Mn(II) ions depend mainly on the pH values and pressure. Figure 4 shows the effect of pressure on ion separation in solutions with different pH values.

Mn(II) ions are removed completely from a solution with pH 3 by the chitosan membrane. Separation decreases when other ions are present. For pH above 5.6 and at a higher pressure the ions are separated only partially, while pressure increases.

The separation properties of chitosan membranes for Cr(VI) change with the pH of the solution. The separation of Cr(VI) ions on chitosan membranes is shown in Figs. 5 and 6.

The efficiency of Cr(VI) ions removal by chitosan membranes depends mostly on the pH of the solution and on the ultrafiltration pressure. For Cr(VI) ions at pH 3.6, the separation efficiency also depends on the time

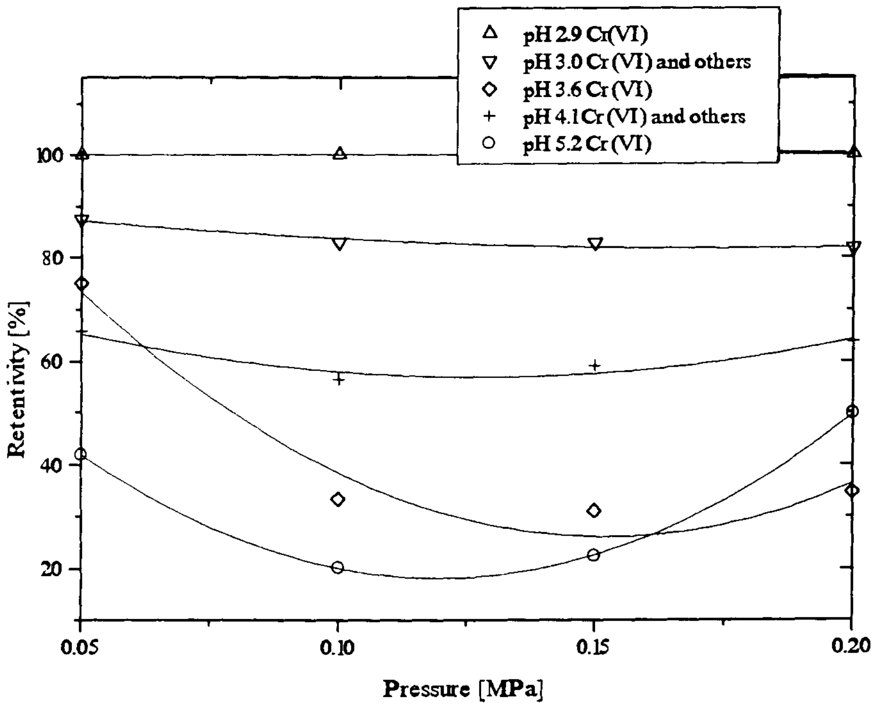

FIG. 5 Cr(VI) ion separation on the chitosan membrane (chitosan 57).

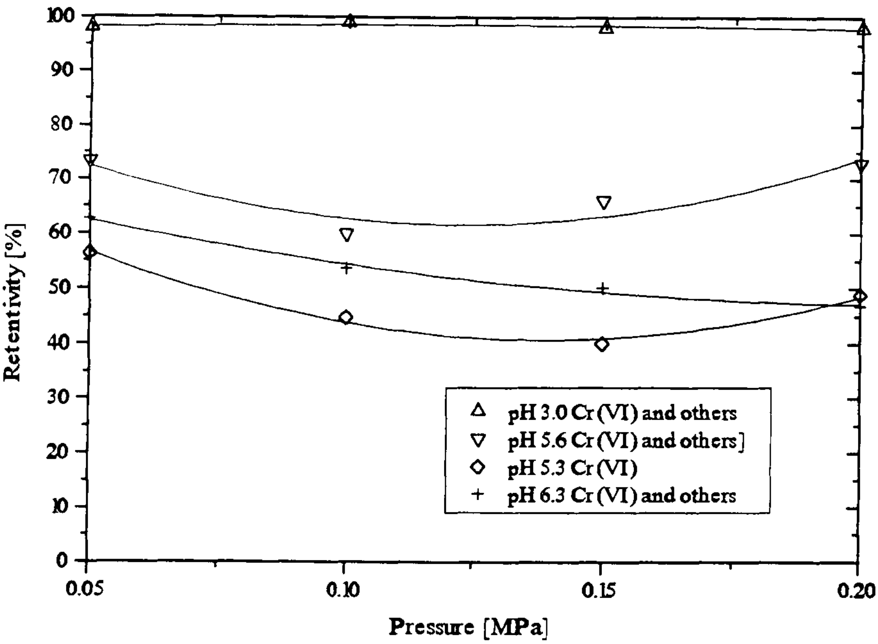

FIG. 6 Cr(VI) ion separation on the chitosan membrane (chitosan 69).

of contact of the solution and the membrane. This time was different due to different hydraulic permeabilities of the tested membranes: membranes with lower permeabilities appeared to be more selective.

It was also observed that as in the case of Fe(III), at pH 3.0 the Cr(VI) ions are absorbed in the membrane. After 70 minutes of ultrafiltration the concentration decreased to 50% in the solution.

A color change of the membrane to green-yellow was observed due to the effect of Cr(VI) absorption.

Separation Properties of Acetylated Membranes

Acetylated chitosan membranes are interesting because of their high resistivity to organic acids and their favorable transport characteristics (Fig. 7). Membranes were completely acetylated and insoluble in a medium with a pH lower than 2. Metal ions separation was carried out in an acidic medium with pH 1.78. The results obtained appeared unsatisfactory. The separation properties for metal ions are shown in Fig. 8.

However, Cr(VI) ions, which are the most difficult to separate on standard membranes, are relatively well separated on acetylated membranes.

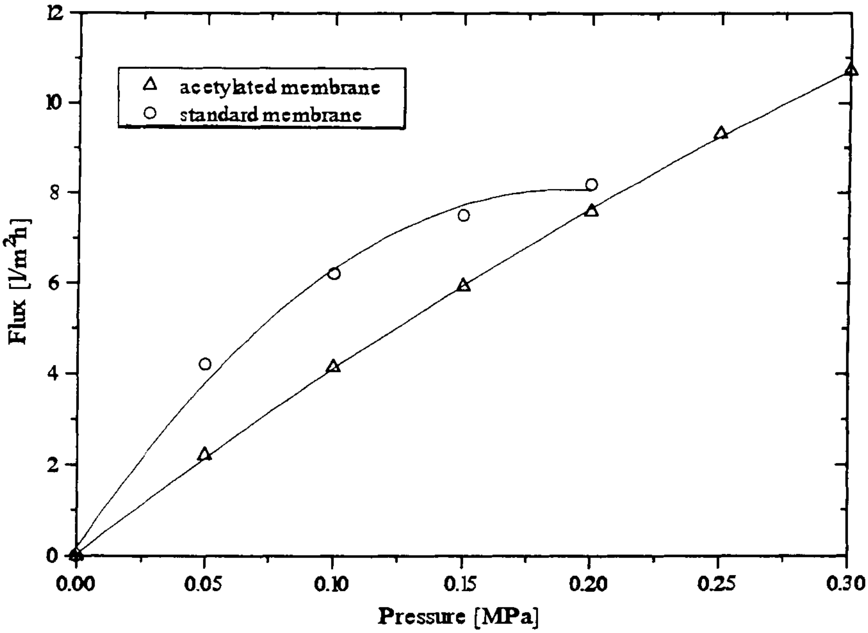

FIG. 7 Transport characteristics of acetylated membranes and the membranes produced by the phase inversion method.

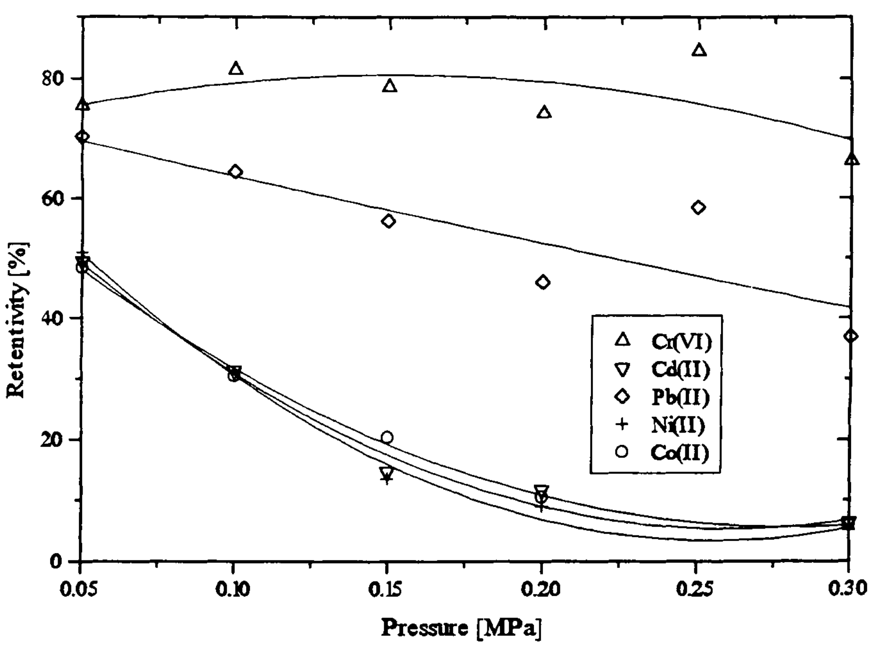

FIG. 8 Separation of metal ions on acetylated membranes.

CONCLUSIONS

From the investigations it follows that:

1. Chitosan membranes produced by the phase inversion method can be applied in the removal of metal ions Cr(VI), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II).
2. Metal ions Cu(II), Cd(II), Co(II), Zn(II), and Ni(II) are separated by the membranes almost completely.
3. In the case of Cr(VI) and Mn(II) ions, the separation depends on pH and process conditions.
4. Acetylated chitosan membranes do not show separation properties in relation to the metal ions being investigated.

REFERENCES

1. R. A. A. Muzzarelli, *Natural Chelating Polymers*, Pergamon Press, 1977.
2. Y. Baba, H. Hirakawa, and K. Yoshizuka, "Synthesis and Adsorption Properties of a Chitosan Derivative for Metal Ions," *Proceedings of the International Conference on Ion Exchange ICIE*, Tokyo, Japan, 1991, pp. 199–204.
3. K. Inoue, K. Yoshizuka, and Y. Baba, "Adsorption of Metal Ions on Chitosan and Its Derivatives," *Ibid.*, pp. 543–548.
4. K. Inoue, Y. Baba, and K. Yoshizuka, "Selectivity Series in the Adsorption of Metal Ions on Resin Prepared by Crosslinking Copper(II)-Complexed Chitosan," *Chem Lett.* pp. 1281–1284 (1988).
5. K. Inoue, Y. Baba, and K. Yoshizuka, "Adsorption of Metal Ions on Chitosan and Crosslinked Copper(II)-Complexed Chitosan," *Chem. Soc. Jpn.*, pp. 1915–1921 (1993).
6. "Membrane für Trennung von Flussigkeiten durch Verdunstung," Patent DE 3600333 (1985).
7. J. Masłowska and T. Nowicki, "Studies on the Utilization of Chitosan to Remove Heavy Metal Ions from Water and Sewage by the "Comp-UF" Method," *Bull. Lodz Tech. Univ.*, pp. 127–138 (1994) (in Polish).
8. V. F. Lee, M.Sc. Thesis, University of Washington, Seattle, USA, 1974.
9. Polish Standard PN-89/A-86850.
10. L. Segal, I. I. Crecly, A. E. Martin, and C. M. Conrad, "An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using X-ray Diffractometer," *Text. Res. J.*, *29*, 786 (1959).

Received by editor August 16, 1996
First revision received January 1997
Second revision received March 1997