

Utilization of Some Starch Derivatives in Heavy Metal Ions Removal

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ABSTRACT: Three types of starch derivatives containing amide groups were used in removal of heavy metal ions from their solutions. These starch derivatives were poly(acrylamide)–starch graft copolymer, carbamoylethylated starch, and starch carbamate. The different factors affecting metal ion adsorption on these substrates, such as pH, metal ion concentration, type of starch derivatives, treatment time, and temperature, were studied. Results obtained indicate that the poly(acrylamide)–starch graft copolymer was a selective adsorbant for Hg^{2+} at pH 0.5–1. The adsorption values of different metal ions on these starch derivatives follow the order of $\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$. The adsorption values depend upon pH, type of starch derivative, treatment duration, and temperature. The adsorption efficiency percentage of metal ions on the three substrates follows the order of carbamoylethylated starch $>$ poly(acrylamide)–starch graft copolymer $>$ starch carbamate. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 45–50, 1998

INTRODUCTION

Synthetic ion exchangers are widely used in the removal of heavy metal ions from industrial water effluent.^{1,2} Our previous articles showed the ability of heavy metal removing from industrial wastewater by using starch derivatives containing carboxyl^{3,4} or phosphate,⁵ or sulphite, phosphate and/or carboxyl groups.⁶ Also, the removal of heavy metal ions was carried out via chelation by using cationic starches.^{7,8}

This work aims to removal of heavy metal ions via chelation on some neutral starch derivatives containing amide groups. These starch derivatives have different structures and contain the same adsorbing group (amide group). The starch derivatives are poly(acrylamide)–starch graft copolymer, carbamoylethylated starch, and starch carbamate. The different factors affecting metal ion adsorption, such as pH, treatment temperature, and duration, as well as the starch deriva-

tive type, were studied. Also, the study included the durability of these starch derivatives for repeated adsorption and desorption of the different metals.

EXPERIMENTAL

Materials

Poly(acrylamide)–starch graft copolymer (780 mmol amide group/100 g sample), carbamoylethylated starch (339 mmol amide group and 81.8 —COOH group/100 g sample), and starch carbamate (465 mmol amide group/100 g sample) were prepared according to reported methods.^{9–11}

Metal Salts

Copper acetate, chloride, sulphate, and acetate of mercury, zinc, nickel, cobalt, cadmium, and lead were of Analar laboratory grade chemicals.

Adsorption of Metal Ions

To a glass-stoppered bottle containing 0.1 g of starch derivative, 90 mL of 0.5M acetic acid–ni-

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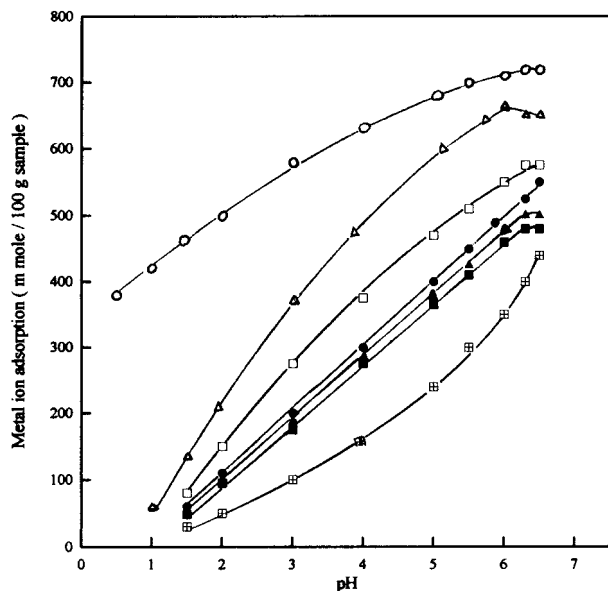


Figure 1 Adsorption of different metal ions (expressed as mmol/100 g sample) on poly(acrylamide)-starch graft copolymer at different pH values: (○) Hg, (△) Cu, (□) Zn, (●) Ni, (▲) Co, (■) Cd, and (⊞) pb.

tric acid (pH 0.5–2) or 0.5M acetic acid–sodium acetate (pH 3–7) and 10 mL of 0.1M metal ion solution were added. The mixture was occasionally shaken for the desired duration and temperature. The adsorption value was calculated by determining the metal ion concentration before and after treatment with starch derivative by titration against standard EDTA.

Desorption of Metal Ions

The treated starch derivative with metal ion was stirred with 50 mL of 0.1N nitric acid for 2 h at room temperature and then filtered, and the metal ion in the filtrate was determined.

The Adsorption Efficiency Percentage

The adsorption efficiency percentage was calculated as follows:

The adsorption efficiency

$$= \frac{\text{the adsorption value}}{\text{starch derivative capacity}} \times 100$$

RESULTS AND DISCUSSION

When poly(acrylamide)-starch graft copolymer was treated with copper acetate, chloride, and sul-

phate, the adsorption values were different. This is due to the dependance of adsorption of any metal ion on the gegen ion. For this reason, all metal salts used in this study were metal acetate.

Effect of PH

Different metal ions were adsorbed on poly(acrylamide)-starch graft copolymer at different pH values (0.5–6.5). Figure 1 shows the adsorption of these metals at different pH values. The data show the following.

1. The adsorption of the metal ions increases with increasing the pH values within the range studied. This due to less stability of the formed chelates in highly acidic medium.
2. The adsorption of the different metal ions depends on the pH value as follows: At pH value 0.5, the only metal ion adsorbed was Hg^{2+} , and the adsorption value was 380 mmol/100 g sample; at pH value 1, the adsorbed metal ions were Hg^{2+} and Cu^{2+} only, and the adsorption values were 420 and 60 mmol/100 g sample, respectively; at pH range 1.5–6.5, all metal ions used were adsorbed with different values, depending on the nature of the metal ion. This phenomenon can be used in selective adsorption of Hg^{2+} from its mixture with other metal ions at pH range (0.5–1).

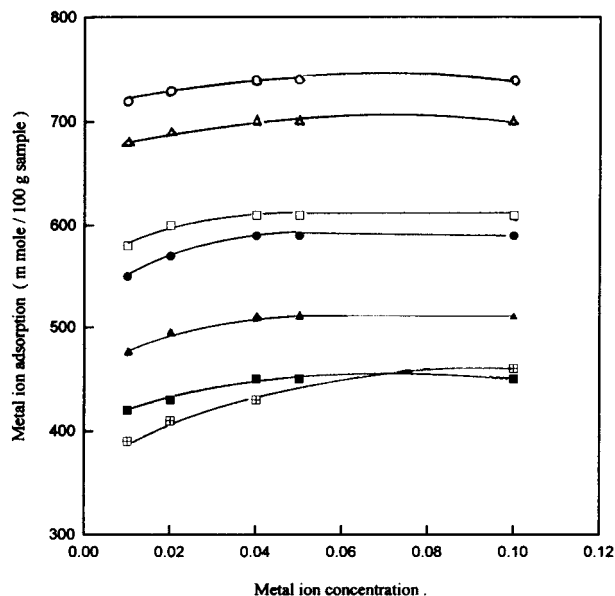


Figure 2 Adsorption values (mmol/100 g sample) of different metal ions on poly(acrylamide)-starch graft copolymer versus metal ions concentration: (○) Hg, (△) Cu, (□) Zn, (●) Ni, (▲) Co, (■) Cd, and (⊞) pb.

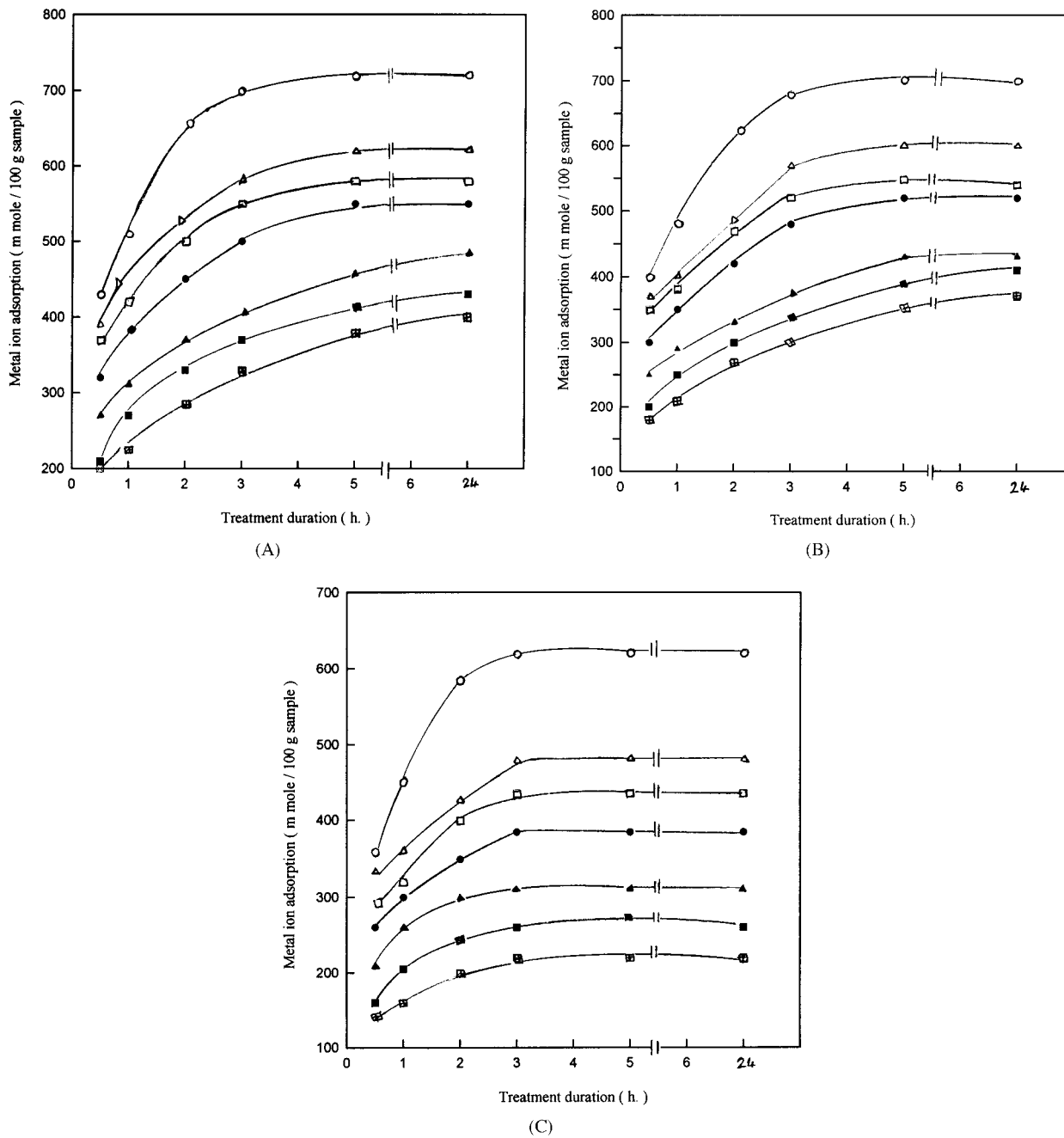


Figure 3 Adsorption of different metal ions (mmol/100 g sample) on poly(acrylamide)-starch graft copolymer at different temperatures and durations: (○) Hg, (△) Cu, (□) Zn, (●) Ni, (▲) Co, (■) Cd, and (⊞) pb.

3. The adsorption values depend on the metal ion used and follow the order of $Hg^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+} > Pb^{2+}$, which is in accordance with Irving-William's series^{12,13} for the stability of various ligands with nitrogen or oxygen as coordinating atoms for divalent transition metal ions.
4. The adsorption efficiency percent of poly(acrylamide)-starch graft copolymer for dif-

- ferent metal ions shows a maximum value of 92.3 for Hg^{2+} and a minimum value of 51.3 for Pb^{2+} , and the other metal ions occur in between. These differences in the adsorption efficiency percentage may be attributed to the different stability constants of the formed complexes between different metal ions and the ligand.¹⁴⁻¹⁶
5. The optimum pH values for adsorption of dif-

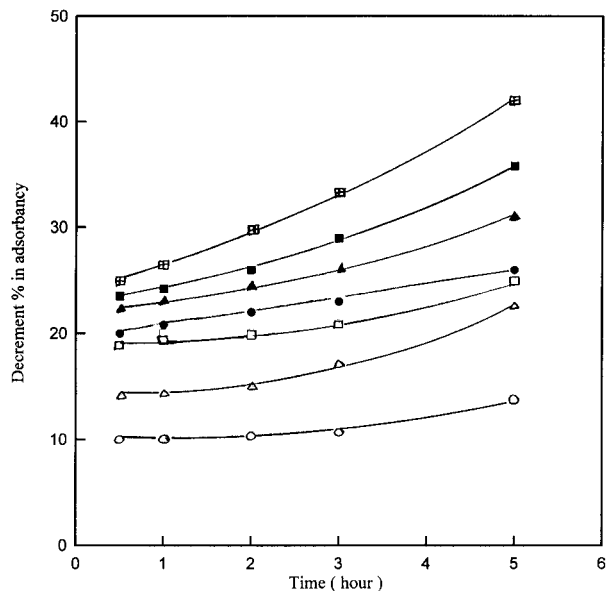


Figure 4 Decrement percentage in adsorption of different metal ions on poly(acrylamide)–starch graft copolymer at various durations on raising the treatment temperature from 20 to 60°C: (○) Hg, (△) Cu, (□) Zn, (●) Ni, (▲) Co, (■) Cd, and (⊞) pb.

ferent metal ions occur in the range of 5.5–6.5, depending on the metal ion used.

Effect of Metal Ion Concentration

Poly(acrylamide)–starch graft copolymer was treated with different concentrations of metal ions. Figure 2 shows the adsorbed amounts of metal ions on using different concentrations. The data show the following.

1. The adsorbed amounts of metal ions increases slightly with increasing the metal ions concentration up to 0.04M and then levels off. This phenomenon occurs with all metal ions used except Pb^{2+} , which increases with increasing the concentration up to 0.1M. The same phenomenon was reported by Chan et al.¹⁷ on adsorption of different metal ions on iminodiacetate cellulosic sorbent.
2. The maximum adsorption efficiency percentage was 94.9% for Hg^{2+} , and the minimum was 59% for Pb^{2+} .

Effect of Treatment Temperature and Duration

The adsorption of metal ions on poly(acrylamide)–starch graft copolymer was carried out at different temperatures (20–60°C) and durations

(0.5–24 h). Figure 3(A–C) shows the adsorption of metal ions at different temperatures and durations.

The data show the following.

1. The adsorption of metal ions increases with increasing treatment duration to reach maximum value of the equilibrium state and then levels off. The maximum adsorption values occur after 5 and 3 h at 20–40 and 60°C, respectively (Fig. 3A).
2. The adsorption value of metal ions decreases on raising treatment temperature. This is due to the higher stability of formed chelates at lower temperatures, as is generally observed for low-molecular-weight complexes. This observation is in agreement with that obtained with Nakamura et al.¹⁸
3. The decrement in metal ion adsorption due to raising the treatment temperature from 20 up to 60°C depends on the metal ion used and the treatment duration. The decrement percentage follows the order of $\text{Hg}^{2+} < \text{Cu}^{2+} < \text{Zn}^{2+} < \text{Ni}^{2+} < \text{Co}^{2+} < \text{Cd}^{2+} < \text{Pb}^{2+}$, as shown in Figure 4, which can be interpreted

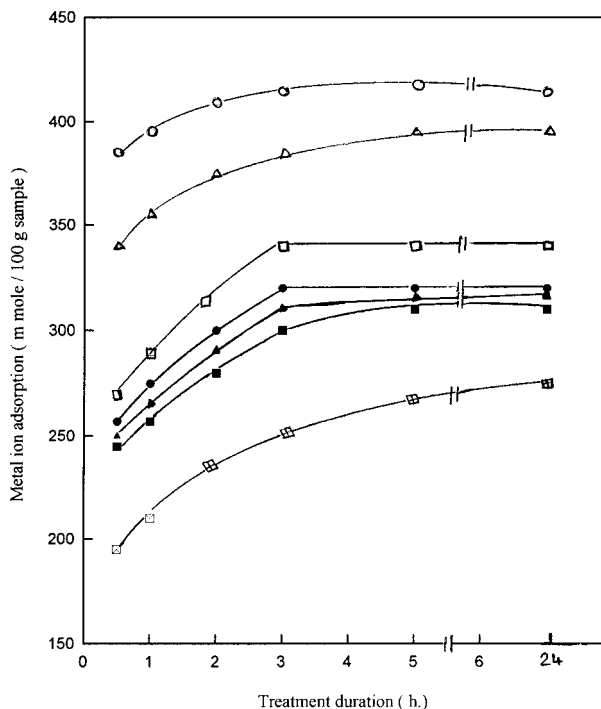


Figure 5 Adsorption of different metal ions (mmol/100 g sample) on carbamoyl ethylated starch at 20°C and different durations: (○) Hg, (△) Cu, (□) Zn, (●) Ni, (▲) Co, (■) Cd, and (⊞) pb.

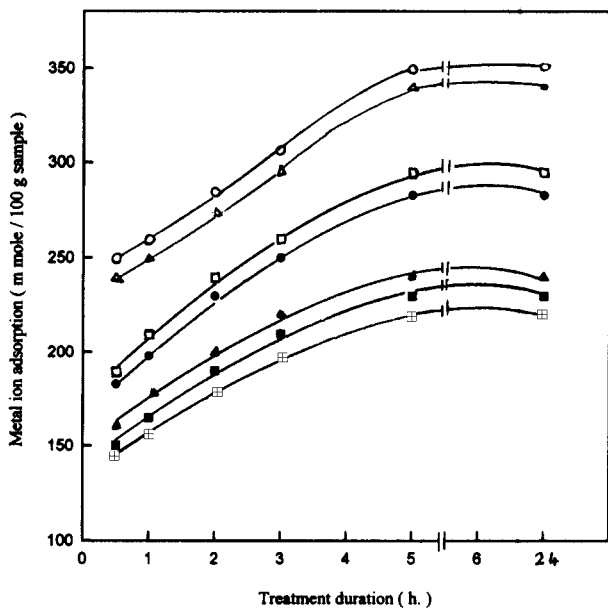


Figure 6 Adsorption values of different metal ions (mmol/100 g sample) on starch carbamate at 20°C and different durations: (○) Hg, (△) Cu, (□) Zn, (●) Ni, (▲) Co, (■) Cd, and (⊞) pb.

in terms of differences in stability of the formed complexes.

Effect of Starch Derivative Type

Adsorption of metal ions was carried out using three types of starch derivatives, namely, poly-(acrylamide)-starch graft copolymer, carbamoylethylated starch, and starch carbamate. Figures 1, 5, and 6 show the adsorption of metal ions

on these three starch derivatives at the optimum conditions obtained.

The data show the following.

1. The adsorption of metal ions increases with increasing the treatment duration to reach the equilibrium state after 5 h.
2. The adsorption of metal ions on the three types of starch derivatives follows the order of $Hg^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+} > Pb^{2+}$.
3. The adsorption is very high within the first half hour of treatment, and the adsorption value (within this period) depends on the metal ion and the starch derivative type. This is in accordance with Chan et al.¹⁷ in their study on iminodiacetate cellulosic sorbent.
4. The adsorption efficiency percentage of metal ions of the three starch derivatives follows the order of carbamoylethylated starch > poly-(acrylamide)-Starch graft copolymer > starch carbamate, as shown in Table I. This phenomenon may be attributed to the difference in structures, the available surface area on these substrates, and the distribution of the adsorbing groups and the distances between them in the three starch derivatives.

Desorption and Readsorption of Metal Ions

The three starch derivatives were used in adsorption of different metal ions and desorbed for several times to see the durability of these substrates.

Table II shows the adsorbancy of the different metal ions on the three substrates after four cycles (adsorption and desorption).

Table I The Adsorption Efficiency Percentage of Different Metal Ions on the Three Starch Derivatives

Metal Ion	Adsorption Efficiency Percentage		
	Carbamoylethylated Starch	Poly(acrylamide)-Starch Graft Copolymer	Starch Carbamate
Hg ²⁺	98.6	92.3	75.4
Cu ²⁺	93.8	79.5	73.3
Zn ²⁺	80.8	74.4	63.6
Ni ²⁺	76.0	70.5	61.0
Co ²⁺	73.6	57.7	51.7
Cd ²⁺	73.6	55.1	49.6
Pb ²⁺	65.3	51.3	47.4

Starch derivative, 0.1 g; metal ion solution, 100 mL; temperature, 20°C; time, 5 h.

Table II The Adsorption of Different Metal Ions on the Three Starch Derivatives After Four Cycles (Adsorption and Desorption)

Metal Ions	Adsorption (mmol/100 g sample)														
	Poly(acrylamide)–starch Graft Copolymer (No. of Cycles)					Carbamoylethylated Starch (No. of Cycles)					Starch Carbamate (No. of Cycles)				
	0	1	2	3	4	0	1	2	3	4	0	1	2	3	4
Hg ²⁺	720	680	560	480	390	415	290	160	70	30	345	170	70	—	—
Cu ²⁺	630	570	480	380	290	395	240	110	47	20	340	163	60	—	—
Zn ²⁺	580	480	380	280	180	340	200	100	47	21	295	142	40	—	—
Ni ²⁺	550	440	350	270	180	330	190	100	47	22	289	130	30	—	—
Co ²⁺	450	400	320	240	140	320	180	95	40	17	240	110	20	—	—
Cd ²⁺	430	370	300	230	135	315	180	95	41	20	230	100	10	—	—
Pb ²⁺	400	320	265	200	110	280	115	95	30	13	220	100	10	—	—

The data show the following.

1. The adsorbed metal ions were easily desorbed by treatment with 0.1M nitric acid at room temperature.
2. The adsorbed amount of the different metal ions decreases after each cycle, and this decrement depends on the used substrate.
3. The stability of these substrates towards adsorption and desorption follows the order of poly(acrylamide–starch graft copolymer) > carbamoylethylated starch > starch carbamate.

The decrease in adsorption capacity of these three substrates may be due to solubility of some highly substituted derivatives within repeated cycles or the decomposition of the substrate, especially in the case of carbamate in the acidic medium used, through the desorption cycle.

REFERENCES

1. F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962.
2. R. Kunin, *Ion Exchange Resins*, 3rd. ed., Wiley, New York, 1958.
3. M. I. Khalil, S. Farag, and A. Hebeish, *Starch*, **43**, 254 (1991).
4. M. I. Khalil, S. Farag, and S. Abdel Fattah, *Starch*, **48**, 270 (1996).
5. M. I. Khalil, A. Waly, S. Farag, and A. Hebeish, *J. Appl. Polym. Sci.*, **43**, 2353 (1991).
6. M. I. Khalil, S. Abdel Rahman, S. Farag, and S. Abdel Fatah, *Egypt. J. Appl. Sci.*, **10**, 900 (1995).
7. M. I. Khalil, S. Farag, and A. Hashem, *Starch*, **45**, 226 (1993).
8. M. I. Khalil and S. Farag, *Starch*, **46**, 17 (1994).
9. A. Hebeish, A. Bayazeed, E. El-Alfy, and M. I. Khalil, *Starch*, **40**, 223 (1988).
10. M. I. Khalil, M. K. Beliakova, and A. A. Aly, *Proceedings of the International Conference on Chemistry and Technology of Fibres and Textiles*, Dec. 10–12, 1996, Cairo, pp. 259–283.
11. M. I. Khalil, S. Farag, Kh. M. Mostafa, and A. A. Hebeish, *Starch*, **46**, 312 (1994).
12. H. Irving and R. J. P. Williams, *Nature*, **162**, 746 (1948).
13. H. Irving and R. J. P. Williams, *Chem. Rev.*, **56**, 271 (1956).
14. J. Blerrm, G. Schwarzenbach, and G. Sillen, *Stability Constants of Metal Ion Complexes*, The Chemical Society, London, Vol. 1, 1958, p. 83.
15. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd. ed., Interscience, New York, 1972, p. 594.
16. S. L. Davadov and N. A. Plate, *Chem. Rev.*, **16**, 195 (1975).
17. W. H. Chan, S. Y. Lame-Leunc, W. S. Fong, and F. W. Kwan, *J. Appl. Polym. Sci.*, **46**, 921 (1992).
18. S. Nakamura, M. Amano, Y. Saegusa, and T. Sato, *J. Appl. Polym. Sci.*, **45**, 265 (1992).