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Preparation of some starch-based neutral chelating agents

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Abstract

Various neutral starch derivatives have been prepared by reacting maize starch with mono- and dimethylol resins based on urea, thiourea, and melamine. The factors affecting these reactions were studied. These factors include curing duration, catalyst, and resin concentrations. The starch derivatives so prepared were used in heavy-metal removal from solutions. The sorption ability of those derivatives depends on resin type and metal ions. The sorption values of different starch derivatives follow the order (a) monomethylol resin–starch > dimethylol resin–starch; (b) thiourea resin–starch > urea resin–starch > melamine resin–starch. The sorption efficiency (%) of starch derivatives increases with increasing nitrogen content, reaching a maximum value and then decreasing. The sorption values of Hg^{2+} (mmol/mol resin) of different starch–monomethylol derivatives at the maximum values were 1135, 2624, and 2538 for urea, thiourea, and melamine derivatives, respectively. This indicates that urea derivatives act as bidentate ligands, while thiourea and melamine act as tridentate ligands. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Starch; Dry state; Urea; Thiourea; Melamine; Chelation; Heavy-metal sorption

1. Introduction

The chemical modification of starch has been extensively studied and the subject has been reviewed [1]. It has been reported [2–5] that introduction of reactive functional groups into the backbone of highly cross-linked starches brings about products that are capable of removing heavy-metal ions from industrial waste water. Thus, anionic starches could be prepared in any of several ways: (1) via reacting cross-linked starch with monochloroacetic acid [6,7]; (2) via alkali treatment of poly(acrylonitrile)–starch graft copolymer [8,9]; (3) via a alkali treatment of poly(acrylamide)–starch graft copolymer [10]; (4) by treating a poly(glycidylmethacrylate)–starch graft copolymer with phosphoric acid [2], and (5) via treatment of a methylolated poly(acrylamide)–starch graft copolymer with acidic salts [11].

On the other hand, cationic starch can be prepared via treatment of starch with dialkylaminoalkyl chloride [12] or a chlorohydrin or a compound with an epoxy group containing amines in the presence of alkali [13], or treatment of a poly(glycidylmethacrylate)–starch graft copolymer [14] or methylolated poly(acrlamide)–starch graft copolymer with different amines [15].

All these starch derivatives have been used in heavy-metal removal [2,8,10,11,13–15]. Recently, Khalil and Farag [16] reported that poly(acrylamide)–starch graft copolymer, carbamoylethylated starch, and starch carbamate acquire high efficiency in absorbing heavy-metal ions from solutions.

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The aim of this work is to prepare some neutral starch derivatives by reacting starch with mono- and dimethylol resins based on urea, thiourea, and melamine. Different factors affecting these reactions such as curing duration, catalyst, and resin concentrations were studied. Also, characterization of the prepared starch derivatives as chelating agents was studied.

2. Experimental

Materials.—Maize starch, urea, thiourea, melamine, formaldehyde triethanolamine, and magnesium chloride hexahydrate were of pure grade. Dihydroxydimethylolethylene–urea (Fixapret-CPN) is a product of BASF. Mercuric, cupric, zinc, cobaltous, cadmium, and lead acetates were of analytical grade.

Methylol derivatives.—Mono- and dimethylol derivatives of urea, thiourea, and melamine were prepared by mixing the nitrogen-containing compounds with formaldehyde using the ratios 1:1.1 and 1:2.2, respectively. The pH was adjusted to pH 9 using triethanolamine, and the mixture was kept at room temperature (rt) for 24 h.

Preparation of starch derivatives.—Starch (10 g) was added to different amounts of methylolated compounds and magnesium chloride (1 g) and mixed well for 10 min using a mechanical stirrer. The mixture was dried in an electric oven at 80 °C and then cured at 150 °C for 10 min. The reaction product was Soxhlet extracted for 12 h using a 7:3 mixture of EtOH and water. The crude material was then dried and analyzed for nitrogen content.

Preparation of starch–dimethylol urea–urea, starch–dimethylol thiourea–thiourea and starch–dimethylol melamine–melamine.—These types of starch derivatives were prepared by reacting starch with dimethylolurea–urea, dimethylolthiourea–thiourea or dimethylolmelamine–melamine mixtures (1:1). Also, starch was reacted with Fixapret-CPN–urea, thiourea or melamine (1:1), using the same procedure described above. The starch derivatives were prepared using different resin–resin base:starch molar ratios (0.05–1). On using molar ratio = *n*, the starch:dimethylolresin:resin base molar ratio was found to be 1:0.5*n*:0.5*n*. The anhydroglucose unit was considered as the starch mole.

Analysis

Nitrogen content (%). The nitrogen content of starch derivatives was determined using the micro-Kjeldahl method [17]. The reaction efficiency (%) (R.E. %) was calculated as follows:

$$\text{R.E. (\%)} = \frac{\text{nitrogen content of prepared sample}}{\text{Theoretical nitrogen content of the reaction mixture}} \times 100$$

Heavy-metal sorption. To a glass-stoppered bottle containing 0.1 g of starch derivatives, 45 mL of 0.5 M AcOH–0.5 M sodium acetate (pH 5.8–6.5) and 5 mL of 0.1 M metal ion solution were added. The mixture was occasionally shaken at rt for 24 h. The sorbed metal ion was calculated from the metal-ion concentration before and after treatment with starch derivatives using standard 0.01 M EDTA solution [17].

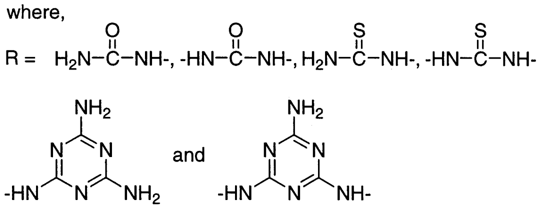
3. Results and discussion

Various types of starch derivatives were prepared by reacting starch with mono- or dimethylolated compounds such as urea, thiourea, and melamine. Different factors affecting these reactions were studied. These factors include curing duration, catalyst concentration, and resin:starch molar ratio. On reacting starch with mono- or dimethylol-containing resins in the presence of magnesium chloride, the following reactions occur:

$$\text{StOH} + \text{RCH}_2\text{OH} \longrightarrow \text{StOCH}_2\text{R} + \text{H}_2\text{O} \quad (1)$$

$$2\text{StOH} + \text{HOCH}_2\text{RCH}_2\text{OH} \longrightarrow \text{StOCH}_2\text{RCH}_2\text{OSt} + 2\text{H}_2\text{O} \quad (2)$$

where,



StOH = starch

These reactions occur beside self-polymerization of the resins used in mono-and dimethylol urea, thiourea and melamine, respectively.

Effect of duration of reaction.—Starch was reacted with monomethylol or dimethylol urea in the presence of magnesium chloride at 150 °C for different times. Fig. 1 shows the nitrogen content (%) of starch derivatives thus prepared. The data show that the nitrogen content of the prepared samples increases with increasing duration of curing up to 20 min and then decreases with longer curing times. This may be explained as follows. At 150 °C the liberated protons have two functions: (1) a catalytic effect of reacting methylol groups with starch hydroxyl groups, and (2) a hydrolytic effect of the formed bonds between the resin and starch. At curing durations of up to 20 min, the catalytic effect is the prevailing reaction and the hydrolytic effect is minor, while at longer durations the hydrolytic reaction became effective, leading to lower nitrogen content for the starch derivative. Accordingly the optimum curing duration is 20 min at 150 °C.

Effect of catalyst concentration.—Starch was reacted with various resins at 150 °C for 20 min using different magnesium chloride concentrations (0.5–3 g/10 g starch). Fig. 2 shows the nitrogen content of different starch derivatives. The data show that (1) the nitrogen content of prepared samples increases with increasing catalyst concentration to reach a maximum value and decreases on using higher concentration, and (2) the maximum occurs at different concentrations depending on the resin type. This maximum occurs upon using 1 g of catalyst in the case of urea and thiourea resins, and 1.5 g in the case of melamine resins. This can be explained on the basis of the liberated acidity, i.e., on using magnesium chloride up to 1 g in the case of urea resins and 1.5 g in the case of melamine resins. The acidity thus generated is quite enough to catalyze the reaction between starch and the resin, while using higher concentrations produces higher amounts of acidity that favor the hydrolytic reaction, which leads to lower nitrogen content. Also, the higher amount of catalyst required to reach a maximum in the case of melamine resins is due to its higher basicity as compared with urea.

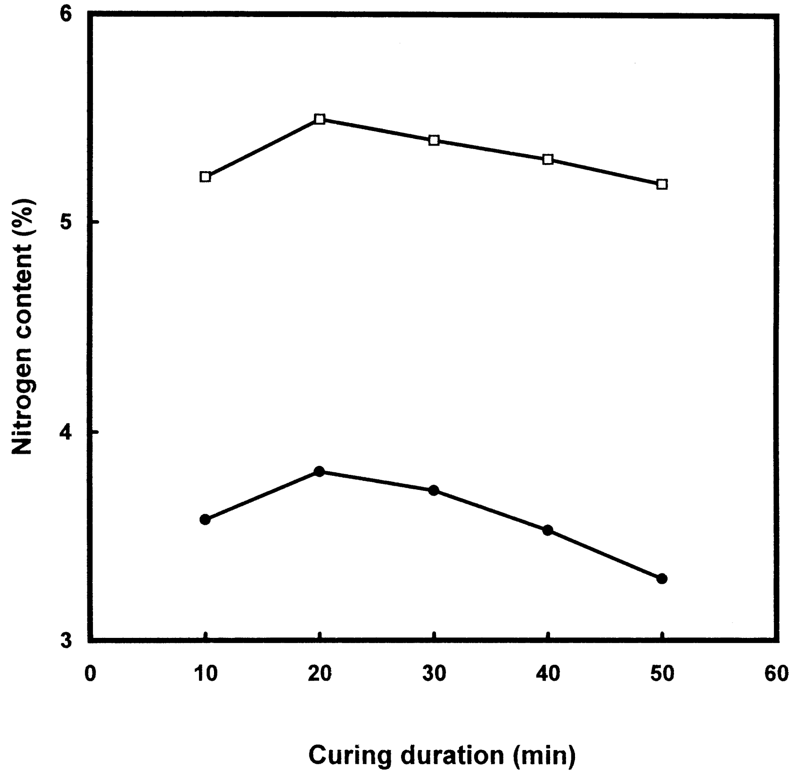


Fig. 1. Nitrogen content of starch urea resin reaction products versus curing duration. -□- MMU, -●- DMU.

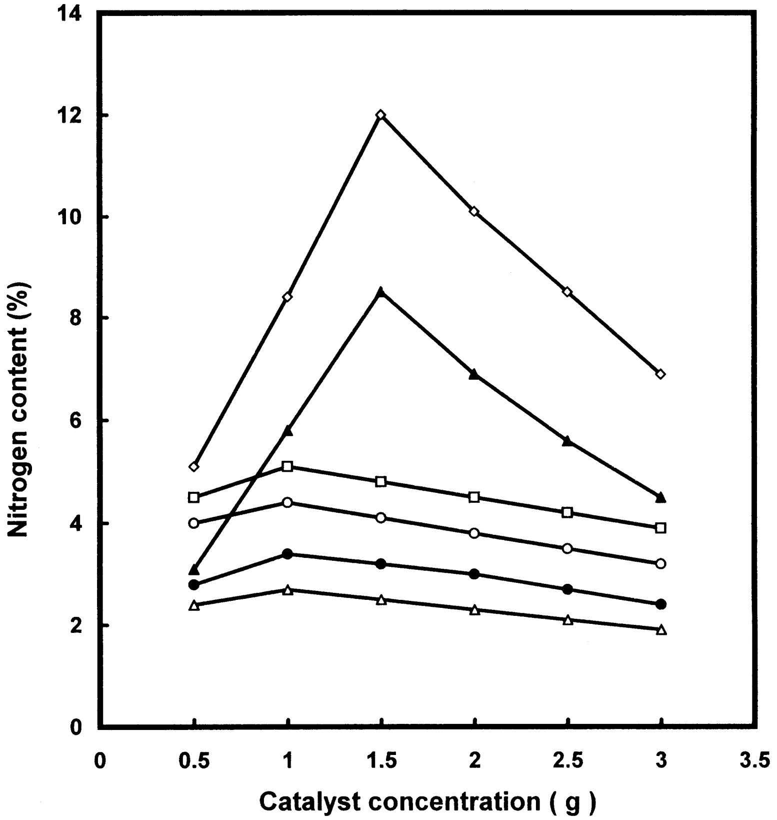


Fig. 2. Nitrogen content of prepared samples versus catalyst concentration. -□- MMU, -●- DMU, -○- MMTU, -△- DMTU, -◇- MMM, -▲- DMM.

Table 1
Nitrogen content (%) and reaction efficiency (%) of various starch derivatives prepared by using different resin:starch molar ratios [a]

Resin:starch M.R.	MMU		DMU		MMTU		DMTU		MMM		DMM	
	Nitrogen (%)	R.E. (%)	Nitrogen (%)	R.E. (%)	Nitrogen (%)	R.E. (%)	Nitrogen (%)	R.E. (%)	Nitrogen (%)	R.E. (%)	Nitrogen (%)	R.E. (%)
0.050	0.845	100	0.845	100	0.81	96.3	0.83	99.0	2.18	87.6	2.39	96.4
0.070	1.127	96	1.162	99.6	1.10	94.3	1.13	97.4	2.40	71.0	3.17	93.2
0.100	1.479	89.4	1.549	94.3	1.43	87.2	1.48	90.8	3.31	69.2	4.16	87.6
0.200	2.100	65.4	2.900	92.9	1.90	60.9	2.50	81.2	5.70	64.4	6.60	75.4
0.250	2.500	64.3	3.333	86.2	2.10	55.3	2.90	77.5	6.80	63.6	7.70	73.3
0.333	3.00	59.8	3.800	77.4	2.50	51.3	3.30	69.0	8.00	59.4	9.40	71.2
0.500	3.900	55.2	5.200	75.8	3.40	50.0	4.20	63.6	10.6	58.3	12.3	69.4
1.000	4.800	40.1	6.000	52.7	4.00	37.0	5.00	46.8	14.0	50.0	15.7	158.3

[a] M.R., molar ratio; MMU, monomethylol urea; DMU, diethylol urea; MMTU, monomethylol thiourea; DMTU, dimethylol thiourea; MMM, monomethylol melamine; DMM, dimethylol melamine; R.E., reaction efficiency.

Effect of resin concentration.—Starch was reacted with various resins using different resin:starch molar ratios (0.05–1.0) in the presence of magnesium chloride at 150 °C for 20 min. Table 1 shows the nitrogen content and reaction efficiency (%) of prepared samples. The data show the following.

(1) The nitrogen content of prepared samples increases with increasing resin:starch molar ratio.

(2) The nitrogen content of the starch–dimethylol resins reaction product is higher than that of the starch–monomethylol resin reaction product. This can be explained as follows. On reacting starch with resin two reactions occur: (a) a reaction between starch and resin and (b) self-polymerization of the resin. Self-polymerized monomethylol resin acquires a lower molecular weight and higher solubility than that of the self-polymerized dimethylol resin. Keeping this in mind, the self-polymerized monomethylol resin will be easily removed through Soxhlet extraction, leading to lower nitrogen content of extracted samples. On the other hand, self-polymerized dimethylol resin acquires higher molecular weight and lower solubility, which is reflected in the high nitrogen content of the extracted samples.

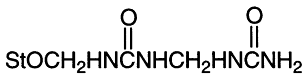
(3) The nitrogen content of starch derivatives prepared by using thiourea resins is lower than that prepared by urea resins. This is valid in the case of mono- and dimethylol resins. This may be due to (a) higher solubility values of self-polymerized thiourea resins than that of urea resins or (b) lower reactivity of thiourea resins than that of urea resins towards reaction with starch.

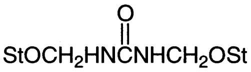
(4) The reaction efficiency (%) decreases with increasing resin:starch molar ratio. This may be attributed to (a) the limited available hydroxyl groups on the starch macromolecule; (b) the cross-linking reactions, which decrease the available surface area and the hydroxyl groups on using higher resin concentrations, and (c) the effect of steric hindrance.

(5) The reaction efficiency (%) on using dimethylol resins is higher than that of monomethylol resin. This is due to the cross-linking effect of the dimethylol resins that serves to lower solubility values of self-polymerized resins.

(6) The reaction efficiency (%) of different starch derivatives follows the order urea resins > thiourea resins > melamine resins. This may be attributed to steric hindrance and difference in solubility of self-polymerized resins, which is higher in the case of melamine resins and lower in the case of urea resins.

Preparation of starch–dimethylol resin–resin base.—Several starch derivatives were prepared by reacting starch with mixtures of dimethylol resin and the resin base (1:1) in the presence of magnesium chloride at 150 °C for 20 min using different mixture–starch molar ratios. On reacting starch with dimethylol urea–urea, dimethylol thiourea–thiourea, or dimethylol melamine–melamine mixtures in the presence of magnesium chloride, the following reaction products are formed.

(1)

$$\mathrm{StOCH_2HN\overset{\overset{\displaystyle O}{\|}}{C}NHCH_2HN\overset{\overset{\displaystyle O}{\|}}{C}NH_2}$$

(2)

$$\mathrm{StOCH_2HN\overset{\overset{\displaystyle O}{\|}}{C}NHCH_2OSt}$$

where StOH = starch

(3) The reaction product of dimethylolurea with urea.

(4) Self-polymerization product of dimethylolurea.

The same reactions occur in the case of thiourea and melamine derivatives. Tables 2 and 3 show the nitrogen content and reaction efficiency (%) of samples thus prepared. (The reaction efficiency (%) calculation is based on reaction product (1) alone.)

The data show the following.

(1) The reaction efficiency (%) of the reaction is very high, meaning that (a) urea, thiourea and melamine were included in the reaction products and cannot be removed with extraction; (b) reactions 1 and 3 are major, and reactions 2 and 4 are minor.

(2) The reaction efficiency (%) of the starch–dimethylol resin–resin base reaction product is higher than that of the starch dimethylol resin.

(3) The reaction efficiency of the starch–Fixapret-CPN–(urea or thiourea or melamine) is higher than that of starch–Fixapret-CPN. This is due to higher cross-linking reactions in the case of Fixapret-CPN, which only seem to lower the reaction extent.

(4) The reaction efficiency (%) of the reaction product follows the order starch – Fixapret-CPN – thiourea > starch–Fixapret-CPN–urea > starch–Fixapret-CPN–

melamine > starch–Fixapret-CPN. This may be attributed to different reactivities of the three compounds (urea, thiourea, and melamine) with Fixapret-CPN.

Characterization of the starch derivatives prepared

Swellability and solubility. All of the starch derivatives thus prepared were, after Soxhlet extraction, water insoluble and were shown to have zero swellability.

Heavy-metal-ion sorption. Different neutral starch derivatives prepared via reacting starch with various mono- and dimethylol derivatives of urea, thiourea, and melamine were reacted with heavy metals. Starch–dimethylol urea–urea, starch–dimethylol thiourea–thiourea, starch–dimethylol melamine–melamine, starch–Fixapret-CPN–urea, starch–Fixapret-CPN–thiourea and starch–Fixapret-CPN–melamine reaction products were utilized in heavy-metal sorption from solution. Metal ions include Hg^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, and Pb^{2+}.

Mono- and dimethylol resins–starch reaction products.—Figs. 3–5 show heavy-metal sorption on various starch derivatives. The data show the following.

(1) The sorption values depend on the metal ion and starch derivatives.

(2) The sorption values on starch derivatives follow the order $Hg^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Cd^{2+} > Pb^{2+}$, which is in accord with the William–Irving series [18] and the finding of our previous report [16]. It was

Table 2

Nitrogen content (%) and reaction efficiency (%) of various starch–dimethylol resin–resin bases prepared by using different resin–resin base:starch molar ratios [a]

Resin–resin base:starch M.R.	St-DMU–U		St-DMTU–TU		St-DMM–M	
	N (%)	R.E. (%)	N (%)	R.E. (%)	N (%)	R.E. (%)
0.050	0.844	99.3	0.83	98.1	2.4	96.0
0.070	1.160	98.0	1.15	98.0	3.2	92.8
0.100	1.590	95.0	1.55	93.4	4.26	88.2
0.200	2.960	92.2	2.80	88.0	6.9	76.4
0.250	3.500	87.7	3.20	82.0	8.2	75.0
0.333	4.100	79.2	3.60	71.5	10.0	72.2
0.500	5.600	75.6	4.40	62.0	12.8	67.7
1.000	6.600	50.93	5.28	43.7	18.0	60.4

[a] DMU–U, dimethylolurea–urea; DMTU–TU, dimethylolthiourea–thiourea; DMM–M, dimethylolmelamine–melamine; St, starch.

Table 3

Nitrogen content (%) and reaction efficiency (%) of various starch–Fixapret CPN–(urea, or thiourea or melamine) reaction products prepared by using different resin–resin base:starch molar ratios [a]

Resin–resin base:starch M.R.	St-Fix. CPN		St-Fix.–U		St-Fix.–TU		St-Fix.–M	
	N (%)	R.E. (%)	N (%)	R.E. (%)	N (%)	R.E. (%)	N (%)	R.E. (%)
0.050	0.77	92.8	0.81	96.1	0.81	96.4	1.60	95.8
0.070	1.02	88.7	1.10	94.2	1.10	94.5	2.1.	91.3
0.100	1.34	84.3	1.50	91.4	1.50	91.7	2.80	86.8
0.200	2.10	71.4	2.60	82.9	2.80	90.0	4.60	76.0
0.250	2.40	67.6	3.00	78.3	3.20	84.4	5.40	73.7
0.333	3.00	67.3	3.60	73.5	3.80	78.4	6.50	69.9
0.500	3.90	65.0	4.60	66.9	4.80	71.1	8.30	65.2
1.000	5.20	56.5	6.20	54.2	6.20	56.0	11.1	55.1

[a] St, starch; Fix. CPN, Fixapret-CPN; FIX–U, Fixapret-CPN–urea; Fix–TU, Fixapret-CPN–thiourea; Fix.–M, Fixapret-CPN–melamine.

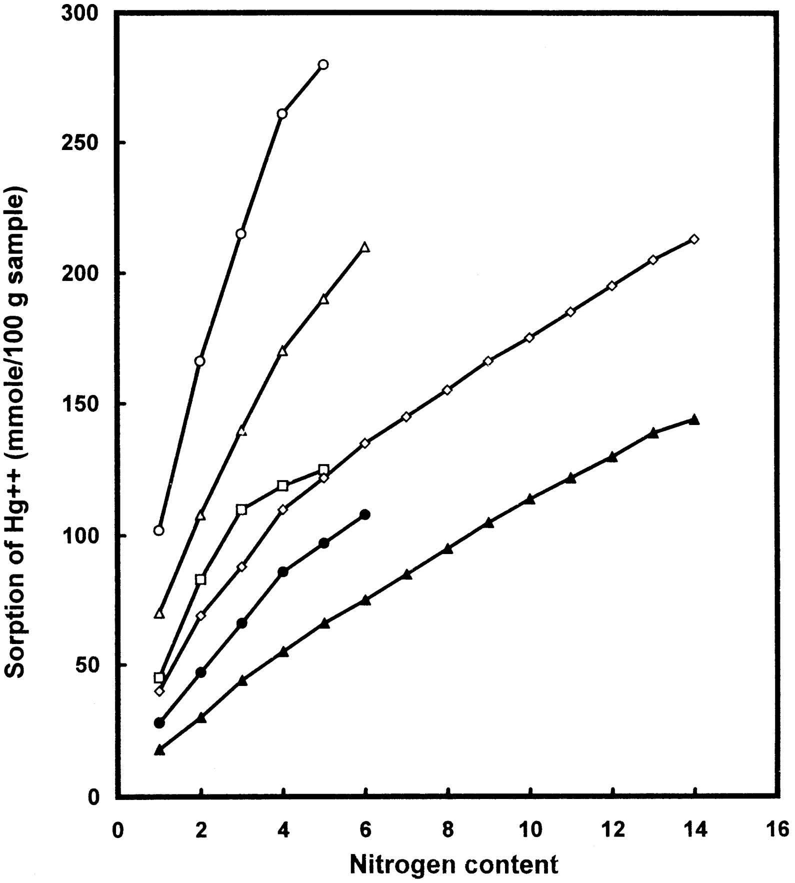


Fig. 3. Sorption of Hg^{2+} on different starch derivatives versus nitrogen content. -□- MMU, -●- DMU, -○- MMTU, -△- DMTU, -◇- MMM, -▲- DMM.

obvious that Hg^{2+} acquires the highest sorption value on these ligands; hence, this metal ion will be used in comparing the sorption behavior of different prepared ligands.

(3) The sorption values of monomethylol resin–starch derivatives were higher than those of dimethylol resin–starch derivatives. This may be attributed to the following (a) the difference in sorption of a substituted and unsubstituted amide group; the sorption value was higher for unsubstituted groups [19–22] due to lack of steric hindrance; (b) different available surface areas on each type are also higher for unsubstituted amide groups in the case of monomethylol derivatives and lower in the case of dimethylol resins, due to higher cross-linking ability of the latter.

(4) The sorption values of metal ions on starch derivatives (either mono- or dimethylol resin–starch reaction products) follow the order thiourea resins > urea resins > melamine resins. This was due to (a) the different abilities of these resins to undergo self-polymerization, which is maximum in the case of melamine resins and minimum in thiourea resins, and (b) the number of donating atoms per resin molecule.

(5) Generally sorption values of mono- and dimethylol resins–starch reaction products follow the order MMTU > DMTU > MMU > MMM > DMU > DMM.

(6) The sorption efficiency (%) on starch derivatives increased with increasing nitrogen content, reaching a maximum value and then decreasing, as shown in Fig. 5. It is known that starch is a polyhydroxy compound and hydrogen bonding greatly affects the available surface area. At lower reaction extent these forces are effective and minimize the available surface area affecting the sorption (%) of metal via chelation. On increasing the reaction extent these forces were minimized and the available surface area increased, leading to higher chances for chelation to reach maxi-

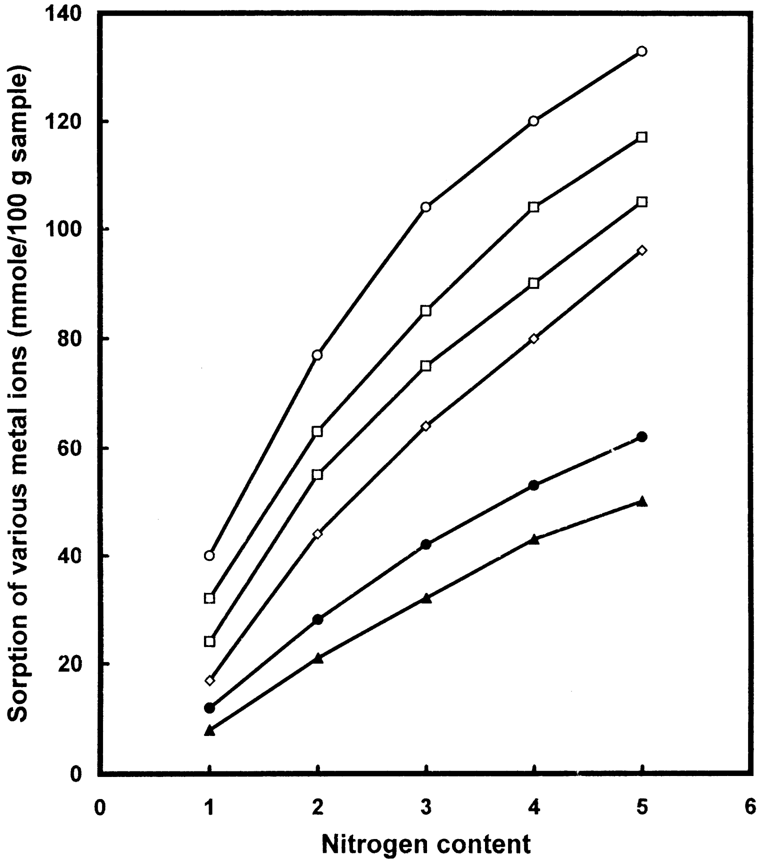


Fig. 4. Sorption of various metals on monomethylolurea reaction products versus nitrogen content. -□- Hg^{2+}, -●- Cu^{2+}, -○- Zn^{2+}, -△- Co^{2+},-◇- Cd^{2+}, -▲- Pb^{2+}.

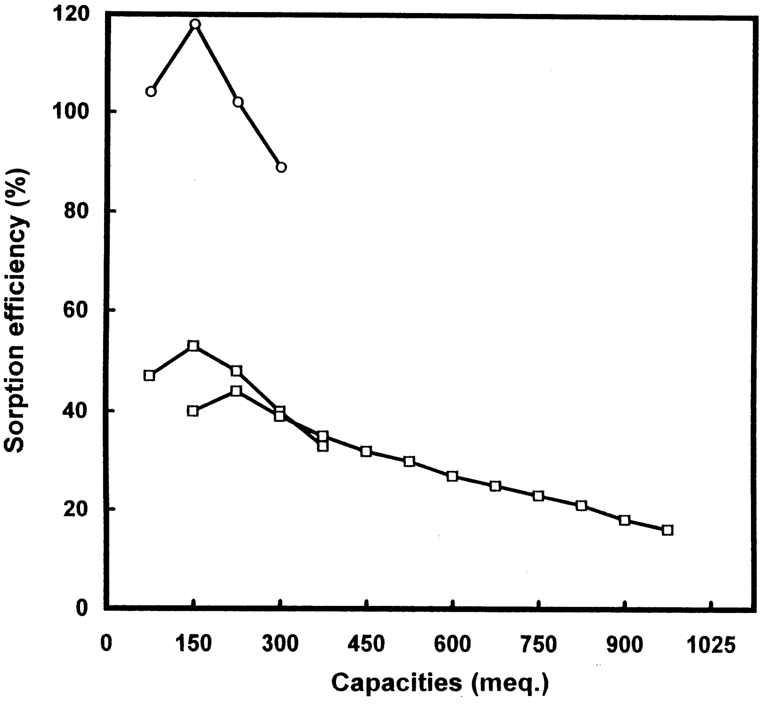


Fig. 5. Sorption efficiency of Hg^{2+} on different substrates versus its capacities. -□- MMU, -○- MMTU, -◇- MMM.

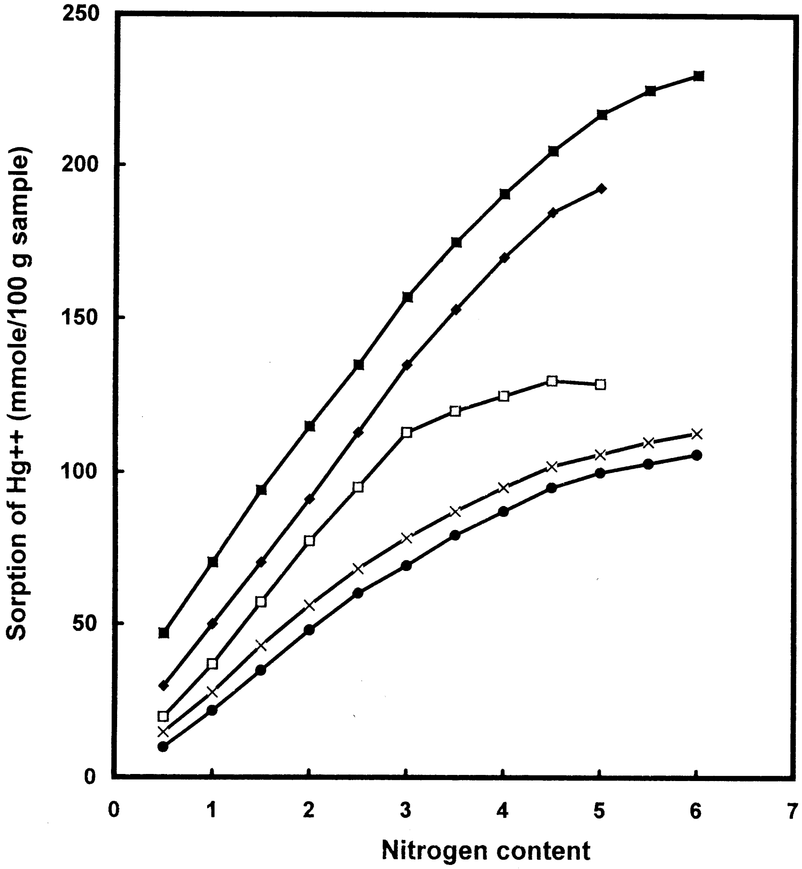


Fig. 6. Sorption of Hg^{2+} on different starch derivatives versus nitrogen content. -■- U/FIX, -◆-FIX, -□-MMU, -X- U/DMU, -●- DMU.

mum sorption. At higher extent of reaction cross-linking occurred, which minimized the available surface area, leading to lower chelation ability.

(7) The sorption values of Hg^{2+} (mmol/resin molecule) at maximum sorption efficiency were 1135, 2624 and 2538 for starch–monomethylol urea, starch–monomethylol thiourea, and starch–monomethylol melamine, respectively. This indicates that there are two donating atoms in these starch derivatives in the case of urea derivatives and three in the case of thiourea and melamine. These atoms are (a) oxygen and one of the nitrogen atoms in the urea derivatives, which is in accord with the findings of Trefonas and co-workers [23,24], who reported that in heavy-metal–ethylene urea chelates, the ligand is bonded to two metal atoms, one via an oxygen atom and the other (less strongly) via a nitrogen atom; (b) one sulfur atom and two nitrogen atoms in thiourea derivations, and (c) three nitrogen atoms, only, in melamine derivations. From these data it can be concluded that thiourea and melamine act as a tridentate ligand, while urea acts as a bidentate ligand only in the starch–monomethylol resin derivatives.

Starch–dimethylol resin–resin base.—It was obvious that sorption of starch–monomethylol resin derivatives was higher than that of starch–dimethylol derivatives. Accordingly the starch–dimethylol resin–resin base derivatives were prepared to minimize cross-linking in these starch derivatives. These were evaluated as chelating agents. Figs. 6–8 show Hg^{2+} sorption of starch dimethylol resin–resin base and starch–dimethylol resin derivatives versus nitrogen content. The data show that: (1) Sorption values of starch–dimethylol resin–resin base derivatives were higher than those of starch–dimethylol resin derivatives. This is due to lower cross-linking and the presence of more unsubstituted amide groups in the former than in the later.

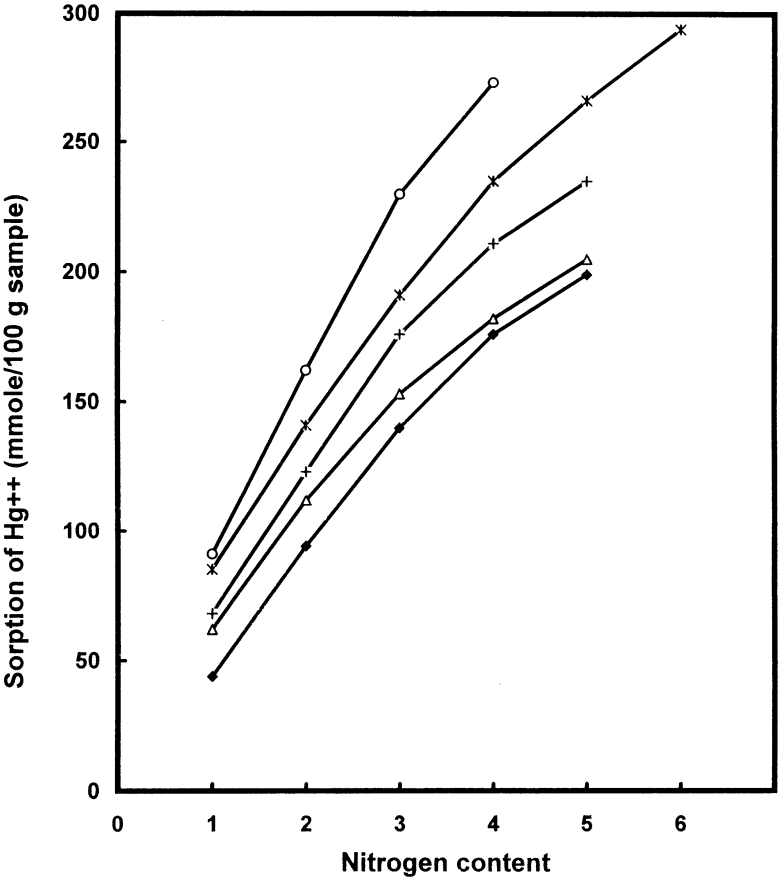


Fig. 7. Sorption of Hg^{2+} on different starch derivatives versus nitrogen content. -○- MMTU, -*-TU/FIX, + TU/MMTU, -△- DMTU, -◆-FIX.

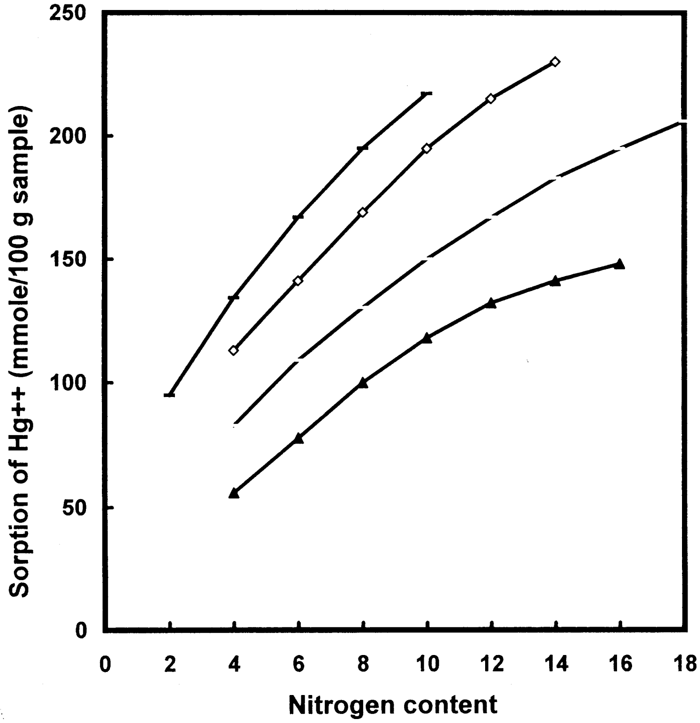


Fig. 8. Sorption of Hg^{2+} on different starch derivatives versus nitrogen content. -M/FIX, -◇- MMM, - -M/DMM, -▲- DMM.

(2) The sorption values of starch–dimethylol resin–resin base derivatives are lower than those of starch–monomethylolated resin derivatives, due to the presence of higher numbers of unsubstituted amide groups in the latter than the former.

(3) Starch–Fixapret-CPN derivatives acquire higher sorption values than those of the starch–dimethylol urea derivative. This may be explained as follows: Fixapret-CPN is a reactant resin that reacts mainly with starch hydroxyl groups with minimal self-polymerization, while dimethylol urea reacts with starch hydroxyl groups and self-polymerizes, forming a three-dimensional network. Keeping this in mind, it will be expected that cross-linking will be very high in the case of the dimethylol urea compared with that of Fixapret-CPN, leading to lower sorption values in the case of the former and higher sorption in the latter.

(4) Starch–Fixapret-CPN–urea derivatives acquire higher sorption values than any other starch urea derivatives, and the sorption values of these derivatives follow the order starch–Fixapret - CPN–urea > starch–Fixapret-CPN > starch–monomethylol urea > starch–dimethylolurea – urea > starch – dimethylol urea derivatives.

(5) The sorption values of thiourea-containing starch derivatives follow the order starch–monomethylol thiourea derivatives > starch – Fixapret - CPN – thiourea > Starch–dimethylol thiourea–thiourea > starch–dimethylol thiourea derivatives.

(6) The sorption values of melamine-containing starch derivatives follow the order starch – Fixapret - CPN – melamine > starch–monomethylol melamine > starch–dimethylol melamine – melamine > starch – dimethylol melamine derivative.

(7) The sorption of starch–Fixapret-CPN–(urea or thiourea or melamine) derivatives follow the order starch–Fixapret-CPN–thiourea > starch – Fixapret - CPN – urea > starch–Fixapret-CPN–melamine.

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