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PREPARATION AND CHARACTERISTIC PROPERTIES OF DITHIOCARBAMATE CHITOSAN, A CHELATING POLYMER

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ABSTRACT

Dithiocarbamate chitosan was obtained by treating chitosan with carbon disulfide in a mixture of ammonia and methanol, and was studied by infrared spectrometry. Dithiocarbamate chitosan having a sulfur content of 7.8% was used to extract metal ions in high yield from acidic, neutral, and alkaline solutions.

INTRODUCTION

Chitosans of animal and fungal origin are effective, solid chelating-agents for transition and post-transition metal ions; the chitosan–glucan complex from *Aspergillus niger* is unsurpassed as far as its ability to retain transition metal ions from dilute solutions is concerned[1–7].

The amino groups of these biopolymers offer the possibility of anchoring various functions to the polysaccharide chain, and several derivatives of chitosan have thus far been prepared[8].

Recently, derivatives of other polymers carrying amino groups have also been studied: thiol and dithiocarbamate functionalities were introduced into polymers prepared by polycondensation of polyethylenimine and cyanuric chloride in the presence of thiourea[9] and into various aminocelluloses treated with carbon disulfide, respectively[10].

The starting raw materials for the preparation of these polymers are synthetic or semi-synthetic. We demonstrate here the suitability of chitosan for introduction of the dithiocarbamate function in a natural aminosaccharide chain, and the efficacy of the derivative for scavenging transition and post-transition metal ions.

EXPERIMENTAL

Chitosan derivatives. — Chitosan from krill (*Euphausia superba*), already described elsewhere[11], having a 60% degree of deacetylation, $[\alpha]_D$ +33°, two h after dissolution in 1% acetic acid at a concentration of 1%, pK 6.6, and 2θ 8°58′ and 19°58′, was used for the preparation of the derivatives. The powder (100–200 mesh, 6.5 g) was treated with carbon disulfide (18 mL), concentrated ammonia (50 mL), and methanol (200 mL) for 5, 24, 70, and 170 h at room temperature. At the end of these timeperiods, the solid was filtered, washed with methanol and ammonia in that order, dried, and stored in a stoppered bottle. After 70 h in the reaction mixture, and not before, the chitosan derivative appears as a blue powder; this color persists even after washing, but fades away the day after the preparation. Some swelling of the derivatives was observed upon contact with water: they do not settle quickly. If their suspensions are brought into contact with a solution of metal ions, immediate precipitation occurs. In strongly acidic solution, the dithiocarbamate develops the detectable odor of hydrogen sulfide.

Instrumentation. — The i.r., u.v., e.p.r., X-ray diffraction, and atomic absorption spectra were recorded with the same instruments and according to the same procedures as described earlier[6]. Sulfur was determined with a LECO 532 automatic titrator.

Metal-ion retention: batch measurements. — The chitosan derivative (100 mg) was stirred with the metal ion solution (25 mL, 0.5mM) for 1 h at room temperature. The sulfates of the following cations were used, Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}. Lead nitrate was also used. Several samples were used after 3, 7, and 10 days from the time of preparation. The approximate pH values of the solutions at the beginning were 0.6, 3.0, 6.8, and 12.0.

Columns. — The columns (10 × 0.6 cm) were fed at the flow-rate of 0.5 mL/min, with 10-p.p.m. solutions of Cu^{2+}. Analyses were performed on 10-mL aliquots. Elution was performed with 0.1M potassium cyanide.

RESULTS AND DISCUSSION

The i.r. spectra of the dithiocarbamate chitosan (DTC-chitosan) exhibit bands

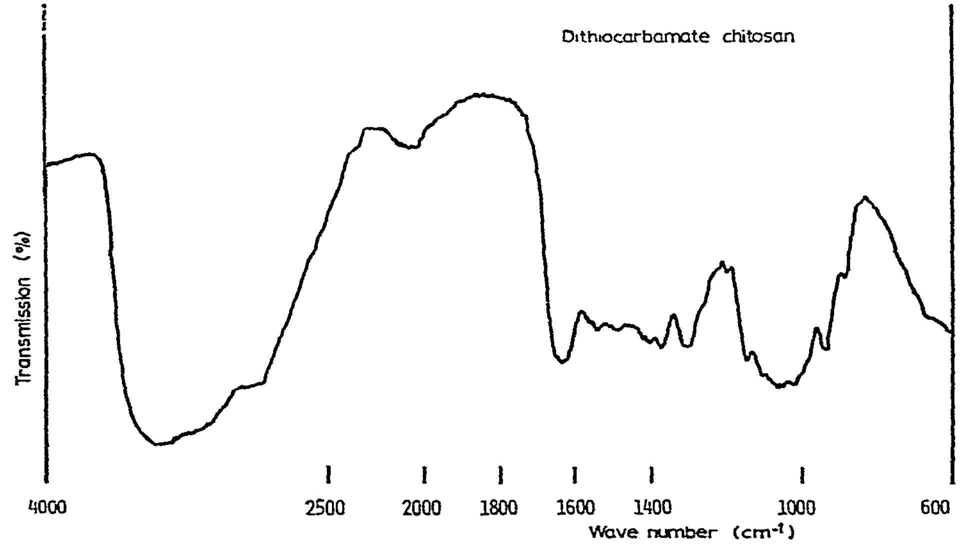

Fig. 1. I.r. spectrum of dithiocarbamate chitosan showing alteration in the region 1400–1550 cm^{-1}.

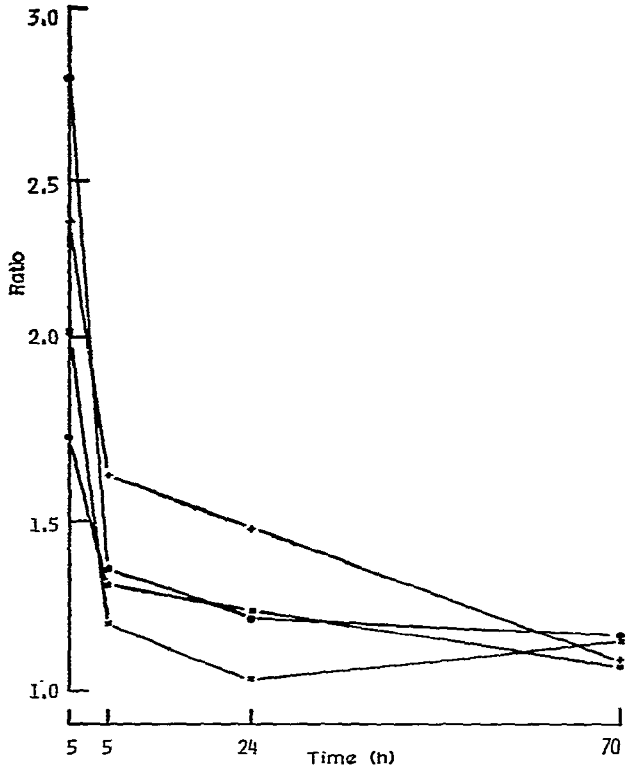

Fig. 2. Ratios between i.r. bands (●) 1650/1480; (×) 1370/1480; (+) 1650/940, and (■) 1370/940 cm^{-1} showing that the formation of DTC-chitosan occurs in <5 h.

at 1480 (assigned to N-C=S) and 940 cm^{-1}, with evidence of generalized alterations in the 1400–1550 cm^{-1} range (Fig. 1). The ratios between the absorption bands at 1650 and 1370 cm^{-1} (not altered with respect to untreated chitosan), and those denoting alterations at 1480 and 940 cm^{-1}, follow the trend in Fig. 2. It may be noted that these ratios drastically decrease during the initial 5 h of reaction, and thus it seems that the DTC-chitosan formation is rather rapid.

TABLE I

2 θ VALUES FOR KRILL CHITOSAN AND DTC-CHITOSAN AFTER VARIOUS LENGTHS OF CONTACT TIME WITH THE REACTION MIXTURE

Time (h)	*2θ*		*d (nm)*	
	Krill	*DTC*		
0	9°13′	19°58′	0.958	0.444
5	8°43′	19°58′	1.012	0.444
24	8°19′	19°58′	1.061	0.444
70	8°13′	19°58′	1.074	0.444

As far as chitin is concerned, the i.r. spectra do not show appreciable differences between the treated and untreated chitin, however the ratios at 1650 and 1480 cm^{-1} decrease from 2.67 for chitin to 2.36 for DTC-chitin. The latter, in fact, possesses limited chelating power. The X-ray diffraction spectra reveal significant alterations depending on the time of contact of chitosan with the mixture. The 2θ reading for the krill chitosan, already reported[11], progressively changes to values listed in Table I. While the e.s.r. spectrum of the original krill chitosan is a featureless single line, those recorded for DTC-chitosan show a sextet of signals whose coupling constant is 85 G. Moreover, five pairs of signals are present having constants 25–30 G. The experiments described here were conducted mostly on DTC-chitosan containing 7.8% S.

Allowing for a moisture content of 5%, the degrees of substitution for the polymer containing 7% sulfur was: 21% dithiocarbamate, 39% free amine, and 40% acetamido; for the polymer containing 11% sulfur was: 35% dithiocarbamate, 25% free amine, and 40% acetamido.

All of the foregoing experimental evidence indicates that chitosan readily reacts with carbon disulfide to produce a derivative possessing distinct characteristics. Modification of the free amino groups of chitosan to give NH-CS-S groups alters the elemental composition of the polymer and the macromolecular conformation as well, mainly because of hydrogen-bond rupture.

Upon stirring, the DTC-chitosan releases to water (pH 9.5) a component of small molecular size, as revealed by u.v.–visible spectrophotometry on the lyophilized water before and after dialysis. One major component of the residue seems to be the ammonium ion arising from dissociation of the ammonium dithiocarbamate, as shown from the strong i.r. spectral bands at 1395 and 650 cm^{-1}.

Transition-metal ions are effectively collected by DTC-chitosan. Numerous measurements by atomic absorption spectrometry showed that both cations and amino complexes in the pH interval tested (5.0–12.0) are totally (95–100%) retained by DTC-chitosan used 4–19 days after its preparation. At pH 3.0, retention is rather low but still appreciable for most of the cations studied. However, tests on Co and Mn performed with DTC-chitosan powder previously kept on filter paper for 3–11 days, indicate that the percentages of retention decrease, presumably because of oxidation, hydrolysis, and loss of hydrogen sulfide: DTC-chitosan should therefore be stored in sealed bottles. The exceptional retention ability of DTC-chitosan is evident in the case of amino complexes of Cu, Ni, Co, and Cd, which are totally retained within one h of contact and impart typical colors to the white powder, as described in Table II.

The capacity of DTC-chitosan was studied as a function of the concentration of metal ion in the range 0.5–10.0mM, at three pH values: 3.0, 6.8, and 12.0 (final values). The results obtained following the batch conditions indicated above are shown in Figs. 3, 4, and 5. Even at low pH (3.0), the capacity of DTC-chitosan is appreciable for a number of cations, especially Co^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+} (more than 5% w/w for the latter two) (Fig. 4). At pH 6.8, the capacities indicated in Fig. 4 at 5mM

TABLE II

COLORS AND RETENTION PERCENTAGES OF THE DTC-CHITOSAN CHELATES OBTAINED FROM 0.5mM SOLUTIONS (100 mg OF 100–200 MESH POWDER STIRRED WITH 25 mL SOLUTION FOR 1 h), AT VARIOUS pH VALUES ADJUSTED WITH SULFURIC ACID OR AMMONIA. COLORS APPEAR IMMEDIATELY AFTER CONTACT

Metal ion	*pH 1*		*pH 3*		*pH 5–7*		*pH 10.5–12*	
	Color	*Retention (%)*	*Color*	*Retention (%)*	*Color*	*Retention (%)*	*Color*	*Retention (%)*
Cr^{3+}	pale yellow	0	grey	4	pale green	96		
Mn^{2+}	pale yellow	25	light brown	13	light brown	93		
Co^{2+}	green	14	dark green	71	dark green	95	brown	100
Ni^{2+}	yellow		green	77	green	100	green	100
Cu^{2+}	brown	90	brown	100	brown	90	dark green, black	100
Zn^{2+}	white		white		white	100	white	
Cd^{2+}	white	10	yellow	100	yellow	100	yellow	100
Pb^{2+}					brown	100		
Ag^{+}					black	100		
Hg^{2+}					light brown milky soln.	100		
UO_2^{2+}					orange	100		

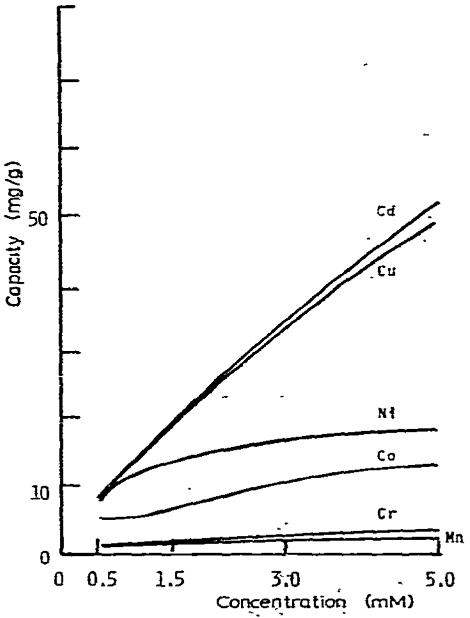

Fig. 3. Capacity of DTC-chitosan for metal ions at 20° and pH 3 ±0.2 as a function of the metal-ion concentration (100 mg/25 mL). Each curve applies to 3 different DTC-chitosans obtained after 5, 24, and 70 h, within the experimental error (±7%).

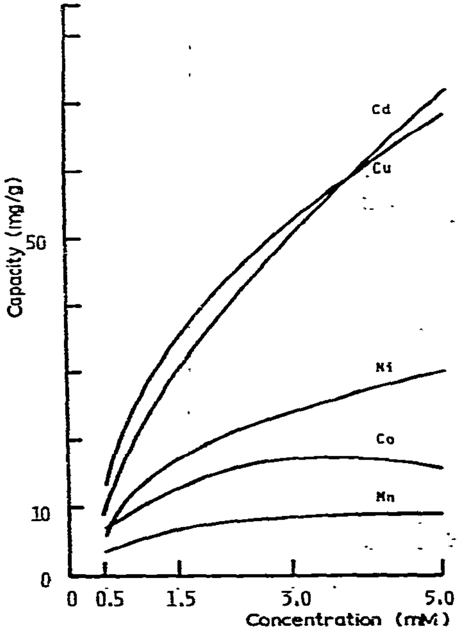

Fig. 4. Capacity of DTC-chitosan for metal ions at 20° and pH 6.8 ±0.2 as a function of the metal-ion concentration (100 mg/25 mL). Each curve applies to 3 different DTC-chitosans obtained after 5, 24, and 70 h, within the experimental error (±7%).

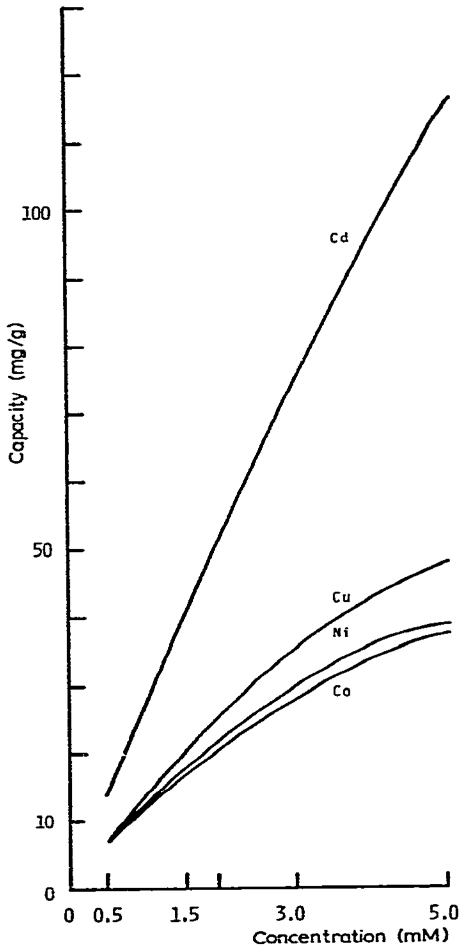

Fig. 5. Capacity of DTC-chitosan for metal ions at 20° and pH 12.0 ±0.2 as a function of the metal-ion concentration (100 mg/25 mL). Each curve applies to 3 different DTC-chitosans obtained after 5, 24, and 70 h, within the experimental error (±7%).

metal-ion concentration are 0.8% for Mn^{2+}, 1.5% for Co^{2+}, 3.0% for Ni^{2+}, 4.0% for Cr^{3+}, 7.2% for Cd^{2+}, and 6.7% for Cu^{2+}. In ammonia solution (pH 12), the respective capacities are: 3.7% for Co^{2+}, 3.8% for Ni^{2+}, 4.7% for Cu^{2+}, and 11.7% for Cd^{2+}. Within experimental error (±7%), the DTC-chitosans obtained after various times of reaction possess the same capacities.

It was therefore anticipated that chromatographic columns would effectively remove metal ions from water. Fig. 6 shows saturation curves obtained with 10 p.p.m. Cu^{2+} solution at pH 9.5 (initial value). At the 10 p.p.m. level, Cu^{2+} is totally removed from a mass of water 100 times larger than the DTC-chitosan in the column; the resulting breakthrough curve is not very steep. The quantitative elution of Cu^{2+}

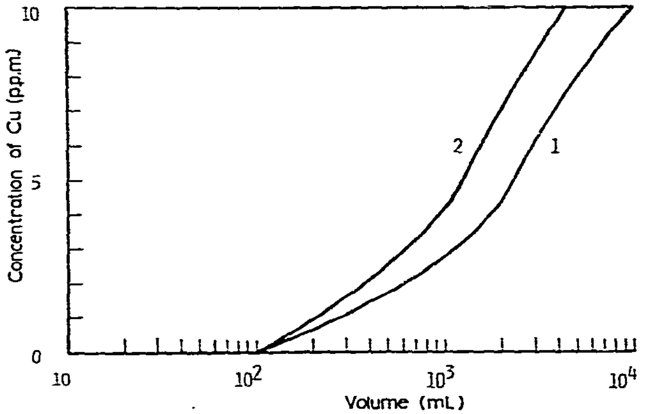

Fig. 6. Breakthrough curves for a 10-p.p.m. Cu^{2-} neutral solution fed to a 0.6 × 10 cm column at a flow rate of 0.5 mL/min; (1) first cycle; (2) second cycle, after elution with 0.1M potassium cyanide and washing.

was performed with 0.1M potassium cyanide: the elution peaks were not very sharp and some taling occurred (30 mL to elute 90% of the Cu^{2+} present). This result demonstrates that, despite of the powerful complexing agent used, the metal ion is very strongly retained on the modified chitosan.

Similarities exist between DTC-chitosan and CDT-celluloses: for instance, the capacities for Cu are: 8 mg Cu/g DTC-chitosan (0.5mM) and 4 mg Cu/g DTC-cellulose (0.125mM); those for mercury are: 25 mg Hg/g DTC-chitosan (0.5mM), and 20 mg Hg/g DTC-cellulose (0.1mM) under comparable conditions[10]. The retention percentage for cobalt at pH 3 is 71 for DTC-chitosan but only 5 for DTC-cellulose; for cadmium at pH 3 is 100 for DTC-chitosan against 65 for DTC-cellulose. A similarity also exists in the high (100% or close) retention percentages for the ammonia complexes at pH 10.0–10.5 (Compare Table II of this work with Fig. 1 of Ref. 10). Where the experimental conditions adopted permit, a comparison may also be made with the polymers obtained from cyanuric chloride treated with polyamines and thiourea: at 0.5mM concentration, copper is completely retained, even at pH 3 (compare Table II and Fig. 3 in this work with Figs. 1 and 2 of Ref. 9), however, the capacity of DTC-chitosan is much higher (50 mg Cu/g DTC-chitosan at 5mM Cu) when compared with 32 mg Cu/g DTC-cellulose at 16mM Cu.

The DTC-chitosan is much easier and less expensive to prepare than DTC-cellulose because the latter requires preparation of aminocellulose from *O*-tosylcellulose; the same may be said for polymers prepared from cyanuric chloride in hazardous solvents.

DTC-chitosan is thus superior to chitosan and to the six derivatives previously described, including thiourea and *S*-acetylmercaptosuccinic anhydride derivatives, as far as manganese, cobalt, and nickel at pH 2.5 and 5.5 are concerned, because their retention values are generally higher for DTC-chitosan than for the derivatives indicated and for chitosan itself (compare Table II in this work with Table I of Ref. 8).

CONCLUSIONS

The regularly distributed amino groups of chitosan allow ready and rapid derivatization with carbon disulfide. The use of commercial chitosan, a natural polyamine, permits the avoidance of such tedious and expensive steps as the amination of cellulose and polycondensation with cyanuric chloride. Dithiocarbamate chitosans having sulfur contents of 7.8% are readily prepared at room temperature within a short time and without any preliminary treatment, thus avoiding polymer degradation. The procedure has advantages over several known methods of substituting the hydroxyl groups of cellulose with amino functions, which cause side reactions and often give low degrees of substitution and breakdown of the polymer chain.

Dithiocarbamate chitosan possesses good retention capacity for transition and post-transition metal ions; even the amino complexes are totally retained under the conditions adopted; this seems to be a peculiar characteristic not matched by other derivatives thus far examined. In any case, this derivative possesses higher capacities than other chelating polymers, with the exception of the chitosan-glucan complex[4-7]. The DTC-chitosan is a useful metal-ion scavenger and may be used effectively to remove a number of metal ions from dilute solutions; it retains cations efficiently even at low pH values, and gives amino complexes with high yields. In all instances, retention occurs very rapidly because of chelation by N and S atoms.

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