Polymer Bulletin 3, 13-17 (1980)

Polymer Bulletin

EDTA Ester of Bead Cellulose
A Fast-Kinetics Chelating Sorbent

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Summary

Crosslinked EDTA ester of cellulose (with 1-1.3 mmole bonded EDTA/g) was synthesized by the treatment of bead cellulose with EDTA bis-anhydride. Compared with the iminodiacetic acid resin, the cellulose EDTA ester exhibits a higher stability of Cu(II) chelates at low pH and a very high sorption rate of Cu(II). The sorbent is stable in neutral and acid medium, but is hydrolyzed by alkalies.

Introduction

Commercially available iminodiacetic acid resins are frequently used for scavenging and separation of metal ions. Their drawback is a small sorption rate and lower stability of their metal complexes reflected in their limited applicability in low pH region (HERING 1967). Insoluble styrene - divinylbenzene copolymers with ethylenediaminetetraacetic acid (EDTA) moiety in pendant groups have been described only recently (KAERIYAMA, SHIMURA 1979). Their synthesis is, however, rather labour- and time-consuming.

Two factors are important for good performance of a complexon sorbent. EDTA complexon grouping should retain six accessible donor sites even after immobilization, this being a prerequisite for the formation of high-stability metal chelates. On the other hand, the properties of the carrier used then decide if the total sorption rates are sufficiently high.

In this communication, the synthesis and properties of bead cellulose EDTA ester are described.

Experimental

Cellulose EDTA ester - ©—EDTA (KAHOVEC 1979)

Suspension of bead cellulose (ŠTAMBERG et al. 1979) in a column was washed successively with distilled water, methanol or absolute ethanol, and ether or benzene, and dried in vacuo at 50°. A stirred mixture

0170-0839/80/0003/0013/$01.00

of 12.4 g dry bead cellulose, 300 ml dry pyridine and 40 g 4,4'-ethylenebis(2,6-morpholinedione) (EDTA bisanhydride; ECKELMAN et al. 1975) was heated in a closed system at 70°C for 24 hours. After cooling, 100 ml of distilled water was added to the reaction mixture, the solid was filtered off and washed several times with the filtrate to remove unreacted EDTA. Finally, the sorbent was washed in a column with distilled water till the coloration and odor disappeared. Approximately 90 ml wet sorbent (ca. 19 g dry matter) was recovered. Nitrogen content ranged from 2.7 to 3.7% corresponding to 0.96-1.32 mmole bonded EDTA/g dry matter. Infrared spectrum exhibited bands at 1640 (COO^-) and 1740 cm^{-1} (ester).

All further measurements were performed on Ⓒ—EDTA of 0.40-0.63 mm wet bead diameter, nitrogen content 2.64%, i.e. 0.94 mmole bonded EDTA/g dry matter, and water regain 3.1 g H_2O/g dry matter (determined by centrifugation method; PEŠKA et al. 1978).

Hydrolytic stability

Ca. 1 ml Ⓒ—EDTA in a column was several times converted to the Na^+ form and back to the H^+ form with with 2M HCl. After that its total capacity for Cu^{++} was determined. The results are given in Table I.

TABLE I

Hydrolytic stability of Ⓒ—EDTA

Conversion to Na^+ form with	Number of cycles (n)	Total Cu^{++} capacity (mmole)		Capacity decrease (%)
		initial	after n cycles	
1M NaCl	5	0.24	0.24	0
0.5M $NaHCO_3$	5	0.24	0.22	8.3
	20-40	0.24	0.21	12.5
0.004M Na_2CO_3	1	0.94	0.62	34.0
0.25M NaOH	2	0.24	0.01	95.8

Total sorption capacity for Cu^{++}

(a) Static: 0.1 g Ⓒ—EDTA and 5 ml 0.04M $CuSO_4$ were shaken at room temperature for 24 h. After filtration, Cu^{++} was determined in the filtrate chelatometrically. Capacity found: 0.90 mmole Cu^{++}/g dry matter.

(b) Dynamic: ca. 1 ml Ⓒ—EDTA was converted to the Cu^{++} form with 60 ml 0.5M $CuSO_4$ (flow rate 1 ml/min).

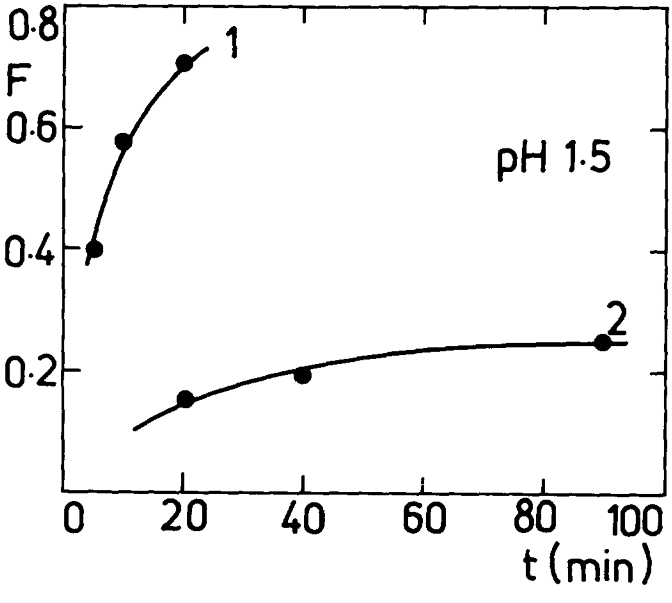
The sorbed copper was eluted with 60 ml 2M HCl, and the sorbent was washed with 100 ml of distilled water. The eluate volume was adjusted to 250 ml with distilled water and Cu^{++} was determined by atomic absorption spectroscopy (AA1, Zeiss Jena). The capacity found: 1.01 mmole Cu^{++}/g dry matter.

Total sorption capacity for Na^{+}

Ca. 1 ml Ⓒ—EDTA in a column was converted to the Na^{+} form with 30 ml 0.004M Na$_2$CO$_3$ (pH 10.7; flow rate 1 ml/min). The sorbed Na^{+} was displaced with 50 ml 1M HCl and determined in the eluate by atomic absorption spectroscopy. Total capacity found 1.54 mmole Na^{+}/g dry matter. After that in the same sample the total Cu^{++} sorption capacity was determined. Found: 0.62 mmole Cu^{++}/g dry matter.

Kinetics of Cu^{++} sorption

was measured by the shallow-bed method (BOYD et al. 1947) in a column of 10 mm i.d. and with ca. 10 mm bed of sorbent in the Na^{+} form. Concentration of entering solution 6.25 mmole Cu^{++}/1, flow rate 50 ml/min. After definite time the flow was interrupted, the sorbent was washed with distilled water and further processed as described above. The sorbed Cu^{++} amount was expressed as a fraction (F) of the total Cu^{++} sorption capacity of the sorbent. The results are given in Fig.1.



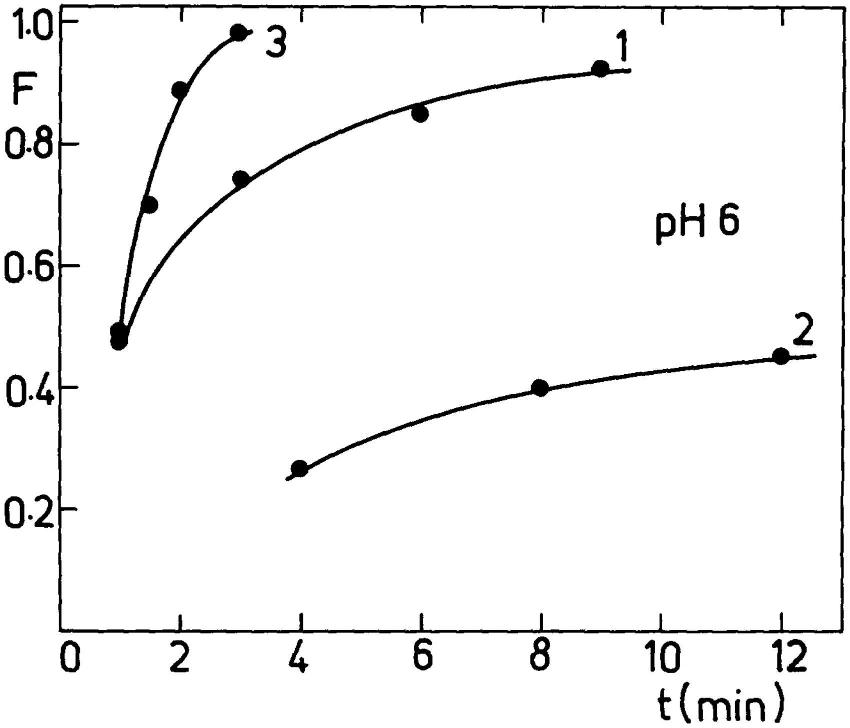
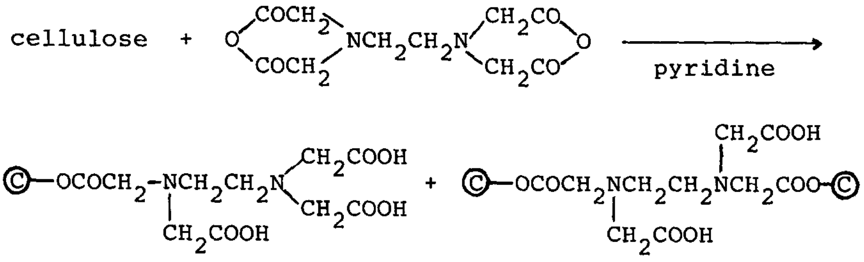


Fig.1 Kinetics of Cu^{++} sorption by cation exchangers in the Na^+ form
1 ©—EDTA; 2 macroporous iminodiacetic acid resin - Lewatit TP 207; 3 sulphonated gel type styrene-divinylbenzene copolymer - Lewatit S 100 (5 mmole Cu^{++}/l, 200 ml/min).

Results and discussion

The synthesis of the novel complexon sorbent is very simple: dry cellulose and EDTA bis-anhydride in the presence of pyridine yield EDTA esters as evidenced by the nitrogen content, and the infrared absorption.



Cellulose crosslinking which occurs in the diester formation is not undesirable as it makes possible a higher substitution degree while retaining insolubility of the cellulose derivative. The extent of cellulose crosslinking is indicated by the bed volume and water regain decrease to 50 and 60%, respectively, of the initial values (before the modification). Diester amount in Ⓒ—EDTA can be estimated by comparing its total sorption capacities for Na^+ and Cu^{++}. Hence, in Ⓒ—EDTA partially hydrolyzed during conversion with 0.004M Na_2CO_3 to the Na^+ form, about 50% of the bonded EDTA is present as diester.

Ⓒ—EDTA forms Cu chelates with the Cu^{++}/bonded EDTA ratio 1:1 by full analogy with EDTA methyl esters (HAY, NOLAN 1975). Ⓒ—EDTA is stable in neutral and acid solutions. It is, however, hydrolyzed in alkaline medium as evidenced by the decrease in capacity (cf. Table I).

The remarkable feature of the novel cellulose derivative is its unusually fast sorption kinetics. In the neutral medium the rate of Cu^{++} sorption with the polymer is higher by an order of magnitude than that with iminodiacetic acid resin and approaches the sorption rate with a strong-acid styrene cation exchanger (Fig.1). On changing pH from 6 to 1.5, the Cu^{++} sorption half-time is extended 6.7 times with Ⓒ—EDTA, but 22 times with the iminodiacetic acid resin. At pH 1.5, the Cu^{++} sorption was still twice as fast as the Cu^{++} sorption with iminodiacetic acid resin at pH 6 (Fig.1). The fast kinetics of sorption is obviously a direct consequence of the strongly hydrophilic and highly porous cellulose skeleton. The results also distinctly indicate the stabler bonding of Cu^{++} to Ⓒ—EDTA compared to that to the iminodiacetic acid resin. Chelating properties and application of the novel complexon sorbent are being examined and will be described in a forthcoming paper.

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Received July 12, Accepted July 14, 1980