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## Hydroxamic Cellulose Fibre as a Chelating Cation Exchanger

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Hydroxamic cellulose fibre with a high content of hydroxamic groups was prepared. The extent of hydroxamation was established by determination of nitrogen. The sorption capacity of the fibre was estimated to be 2.1 mekv/g. The hydroxamic cellulose fibre represents a selective sorbent for fast preconcentration of traces of ions. The effect of the mass of the sorbent, salt effect and contact time on sorption, were studied by using 5—30 mg of the hydroxamic cellulose in 25 ml from 1 to 10 ppm iron(III) solutions. Preliminary results show that hydroxamic cellulose may be used in environmental analytics.

### INTRODUCTION

Solid chelating ionic exchangers with cellulose as a base have often been used recently for preconcentration and determination of traces of ions in environmental analytics. A number of compounds with different chelating groups such as: salicylic acid<sup>1,2</sup>, ( $\beta$ )-alanine-*N,N*-diacetic acid<sup>3</sup>, 8-hydroxyquinoline<sup>4</sup>, 1-(2-hydroxyphenylazo)-2-naphthol<sup>5,6</sup>, 1,2-dihydroxybenzene-3,5-disulphonic acid<sup>7</sup>, o-aminophenol, 1-(2-hydroxyphenylazo)-2-naphthol, 1-(2-hydroxyphenylazo)-2-naphthylamine-*N,N*-diacetic acid<sup>8</sup>, chromotropic acid<sup>9</sup>, *NN'*-ethylenedi-(*o*-hydroxyphenyl)glycine, quinalizarin, arsenazo III, 1-(2-hydroxyphenylazo)-2,4-phenylenediamine-*N,N,N'*-tetraacetic acid<sup>10</sup>, and iminodiacetic acid<sup>11,12</sup> were prepared and examined.

The synthesis of a poly(hydroxamic acid) ion exchange resin from cross-linked poly(acrylonitrile) is described<sup>13</sup>. A hydroxamized cellulose powder with a low content of hydroxamic groups was prepared from a starting material of carboxy-cellulose containing about 6 wt. % of carboxyl groups<sup>14</sup>.

In this paper we wish to report the preparation and some analytical properties of chelating cellulose with a high content of hydroxamic acid as a functional group.

### EXPERIMENTAL

#### Chemicals

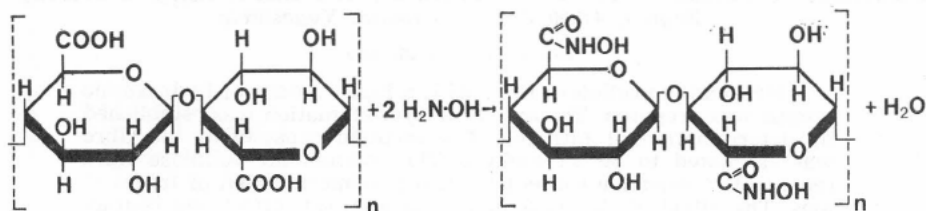
Oxidized regenerated cellulose, Surgical (Johnson Johnson, New Jersey, USA) with about 18 wt.% carboxy groups was used as a starting material for the preparation of hydroxamized cellulose. Hydroxamized cellulose fibre was prepared as subsequently described. Hydroxylamine hydrochloride and methanol were of Merck p. a. grade. All other chemicals were of analytical grade and were used without further purification. The water used in all experiments was redistilled from aqueous acidified potassium permanganate solution.

### Methods

The structures of the products were established by elemental analysis and spectral data. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer Model 457 using KBr pellets. Water content was determined gravimetrically after the samples had been dried 20 hours at room temperature in a vacuum thermostat. Sorption of iron(III) ions was followed spectrophotometrically at 480 nm with a Zeiss-Opton spectrophotometer PMQ II using ammonium thiocyanate as a reagent<sup>15</sup> and 1.000 cm quartz cells.

### Preparation of hydroxamized cellulose

Hydroxylamine hydrochloride (3.63 g) was dissolved in 40 ml of cooled anhydrous methanol and neutralized with an equimolar quantity of sodium methylate (2.81 g) dissolved in 50 ml of methanol.



Scheme of preparation

The mixture was cooled for 2 hours in a refrigerator and precipitated sodium chloride was filtered off.

Surgical cellulose fibre (Celuronic acid) (1.3 g) was suspended in 20 ml of methanol cooled down to 4°C and added slowly to the cold hydroxylamine solution. The mixture was stirred for 5 hours at room temperature and then allowed to stand in a refrigerator overnight.

The fibrous mass was decanted, washed with 20 ml methanol, filtered off and washed 5 times with 20 ml methanol. The product was dried in air and stored in vacuum desiccator. The water content was usually 3.5%.

Characteristic IR bands (KBr): 330–3600 (OH), 2900 (CH, CH<sub>2</sub>), 2710 (NH), 1735 (C=O), 1550–1700 (C=O, NH), 1420 (CH<sub>2</sub>), 1290, 1240 and 800 cm<sup>-1</sup>.  
N content: 2.98%

### RESULTS AND DISCUSSION

#### Sorption capacity

The IR spectra, nitrogen content and colored reaction of iron(III) ions with the product indicate that hydroxamic groups were incorporated into the anhydroglucose unit of the cellulose molecule. The yield is 12.6 wt. % CONHOH. According to the nitrogen content the sorption capacity may be estimated as 2.13 mekv/g of the dried sorbent.

#### Solubility of the fibres

The fibres of the sorbents are not soluble in neutral and acidic medium. It is soluble in alkaline solutions and subsequent hydrolysis of the hydroxamized cellulose was observed. Further experiments are in progress to throw more light on the events that take place in this system after hydroxamized cellulose is dissolved in alkaline solution.

#### Limit of identification and selectivity for some ions

Some of metal ions with hydroxamic cellulose forming colored products<sup>16</sup>. Hydroxamic cellulose may be used as an analytical reagent and/or as a sorbent.

For such ions the identification limits were estimated by the »resin spot test« method<sup>17</sup> applying semistatistical analysis<sup>18</sup>. The obtained values for identification limits are:  $5.3 \times 10^{-7}$  g  $\text{Au}^{3+}$ ,  $1.3 \times 10^{-6}$  g  $\text{Cu}^{2+}$ , and  $8.0 \times 10^{-7}$  g  $\text{Fe}^{3+}$ . The colour of the products were different: red-brown ( $\text{Fe}^{3+}$ ), yellow-green ( $\text{Cu}^{2+}$ ) and gray ( $\text{Au}^{3+}$ ). The following ions do not give visible products with hydroxamized cellulose at a concentration of 10  $\mu\text{g}/0.05$  ml:  $\text{Ag}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{La}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Th}^{4+}$ ,  $\text{Ti}^{3+}$ ,  $\text{UO}_2^{2+}$  and  $\text{Zr}^{4+}$ .

### Salt effect

Effect of different salts on the sorption of iron(III) ions on hydroxamic cellulose is shown in Table I. It is clear that some of the salts such as  $\text{CdCl}_2$ ,  $\text{KCl}$ ,  $\text{LaCl}_3$ ,  $\text{Th}(\text{NO}_3)_4$ ,  $\text{UO}_2(\text{NO}_3)_2$ , and  $\text{ZrOCl}_2$  increase the sorption of iron(III) ions on the hydroxamic cellulose.  $\text{AgNO}_3$  exhibits no effect, however  $\text{Al}_2(\text{SO}_4)_3$  showed a small decreasing effect. In the presence of  $\text{Cu}(\text{NO}_3)_2$  the sorption of iron(III) ions is lacking probably because of strong sorption of copper(II) ions.

TABLE I

The Effect of the Salts on the Sorption of Iron(III)-ions on Hydroxam Cellulose

Salt		mg of the sorbent in 25 ml	iron(III)* sorbed $\mu\text{g}/\text{ml}$
Formula	mg in 25 ml		
—	—	20.0	3.39
$\text{AgNO}_3$	20.0	21.2	3.39
$\text{Al}_2(\text{SO}_4)_3$	20.5	20.5	3.11
$\text{CdCl}_2$	20.0	20.4	4.73
$\text{Cu}(\text{NO}_3)_2$	20.0	21.0	0.00
$\text{KCl}$	21.5	20.5	4.22
$\text{LaCl}_3$	20.8	20.5	4.73
$\text{Th}(\text{NO}_3)_4$	21.2	20.1	4.69
$\text{UO}_2(\text{NO}_3)_2$	20.5	20.0	3.90
$\text{ZrOCl}_2$	21.0	20.8	4.10

\* In all experiments the starting concentration of iron(III) was 5.95  $\mu\text{g}/\text{ml}$

### Sorption characteristics of the hydroxam cellulose

Hydroxamic cellulose is a hydrophilic very porous fibre like chelating ionic exchanger. Our qualitative tests show that it is a selective sorbent with special affinity for preconcentration of iron(III) ions. Sorption of iron(III) ions from acidic solution was a very fast process as is shown in Figure 1. In this experiment iron(III) ion concentration was 5.86 ppm with 5.0—5.2 mg of the sorbent. The sorption is affected by the quantity of sorbent quantity as is shown in Figure 2. The larger amount of the sorbent in same shaking time sorbed larger amount of iron(III)-ions. The optimal conditions for the sorption of iron(III) ions on hydroxam cellulose are the subject of a study which is in progress in our laboratory.

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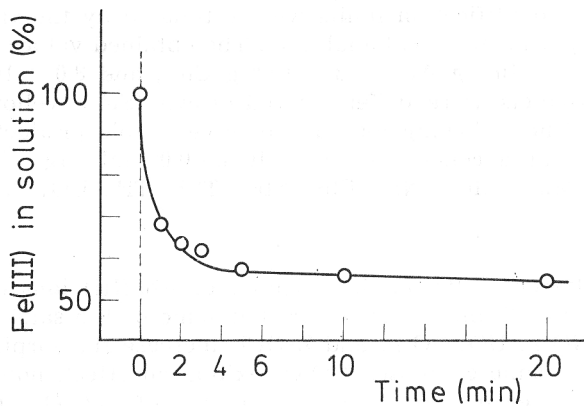


Figure 1. The sorption of iron(III)-ions on hydroxamic cellulose as a function of time. Starting concentration of iron(III)-ions was  $5.86 \mu\text{g/ml}$ . Mass of the sorbent was  $5.0\text{--}5.2 \text{ mg}$  in  $25 \text{ ml}$ .

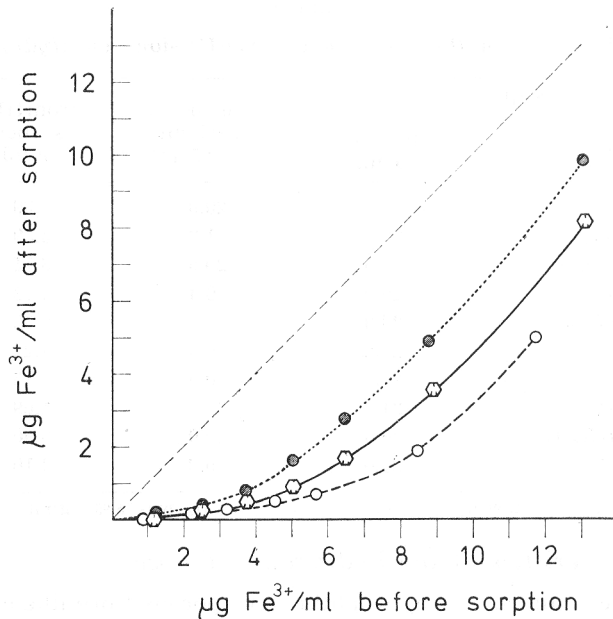


Figure 2. Effects of the mass of the sorbent on the sorption of iron(III)-ions on hydroxamic cellulose.  $\square$  =  $30.0\text{--}31.0 \text{ mg}$  of the sorbent;  $\circ$  =  $20.0\text{--}21.6 \text{ mg}$  of the sorbent;  $\bullet$  =  $9.8\text{--}12.0 \text{ mg}$  of the sorbent. Shaking time was  $10 \text{ min}$ .

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### SAŽETAK

#### Vlakna hidroksam celuloze kao novi kelirajući kationski izmjenjivač

V. Grdinić i N. Kujundžić

Pripremljena su vlakna hidroksam celuloze iz karboksiceluloze s visokim sadržajem hidroksamskih skupina. Određivanjem sadržaja dušika ustanovljen je postotak hidroksamacije i procijenjen sorpcijski kapacitet vlakna koji iznosi 2,1 mekv/g. Vlakna hidroksam celuloze predstavljaju selektivni sorbens za brzo prekoncentriranje tragova iona. Efekt mase sorbensa, stranih soli i trajanja kontaktiranja sakupljanje je ispitan primjenom 5—30 mg sorbensa u 25 ml otopine 1—10 ppm željeza(III). Preliminarna ispitivanja pokazuju potencijalnu mogućnost primjene hidroksam celuloze u analitici prirodnih sustava.

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