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Synthesis of a New Cellulose Ion Exchanger and Use for the Separation of Heavy Metals in Aqueous Solutions

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Abstract: Ion exchange resin based on cellulose has been synthesized to separate the heavy metals, such as Pb, Cd, Co, Cu, Fe, Ni, Zn, and Cr in aqueous solutions. The total ion exchange capacity (IEC) of resin synthesized was determined $3.3\,\mathrm{meq}\cdot\mathrm{g}^{-1}$ as wet and $4.1\,\mathrm{meq}\cdot\mathrm{g}^{-1}$ as dry and average swelling percentage as 19.8. Sodium trimetaphosphate was used as an elution agent for the removal of heavy metals. Distribution coefficients of these elements have been determined regarding five different concentrations of sodium trimetaphosphate ($3\cdot10^{-3}$ M; $5\cdot10^{-3}$ M; 0.01 M; 0.05 M; 0.1 M) on the this resin. By considering these distribution coefficients, the separation of heavy metals has been performed with $5\cdot10^{-3}$ M sodium trimetaphosphate at room temperature. Qualitative and quantitative determinations were realized by ICP. This study has been indicated that the resin synthesized has preferable properties.

Keywords: Cellulose ion exchanger, heavy metals, sodium trimetaphosphate, ion exchange, ICP

INTRODUCTION

Cellulose ion exchangers are made by attaching substituent groups with basic or acidic properties to the cellulose molecule, usually by etherification or esterification reactions. Although similar to ion exchange resins in ion

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exchange properties, they are much finer and present a larger surface. Their porous structure permits the rapid entrance.

On the other hand, the removal of heavy metals from aqueous solutions is extremely important to ensure environmental protection. The separation of heavy metals from each other is also important for an economical aspect. The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the environment. Major sources of heavy metals in the environment include metal extraction, metal fabrication, paints and pigments, as well as the manufacture of batteries.

There are a number of techniques such as precipitation, adsorption, extraction, and ion exchange for the removal of heavy metals from aqueous solutions. However, ion exchange has been used more extensively than other technique because it is an effective and simple method.

In recent years, many cellulose ion exchangers have been prepared. Hebeish and El-Hilw synthesized diethylaminoethyl cotton-g-poly (methacrylic acid) for use as ion exchanger. Then, they investigated the ability of the ion exchanger to remove metal ions from aqueous solutions (1). Baouab et al. reported on the preparation of cationized cotton fiber by treating alkali cellulose cotton fibers with epoxy propyltrimethylammonium chloride (EPTMAC) in a nonaqueous medium and its use as support for the immobilization of pollutant dyes (2). Hebeish et al. prepared ion exchange cotton fabrics containing amino and carboxylic groups via polymerization of glycidyl methacrylate, dimethylaminoethyl methacrylate, and acrylic acid with cotton fabric using cellulose thiocarbonate along with different oxidants, namely Cr^{+6}, V^{+5}, Mn^{+4}, Cu^{+2} ion, as well as ferrous-hydrogen peroxide redox system. Furthermore, they performed characterization of the prepared ion exchanger (3). Yu et al. prepared thiol cotton fiber and investigated adsorption of 11 trace heavy metals (Bi^{+3}, Sn^{+2}, Ag^{+}, Cu^{+2}, In^{+3}, Pb^{+2}, Cd^{+2}, Zn^{+2}, Co^{+2}, Ni^{+2}, Tl^{+}) on this ion exchanger (4). Waly et al. synthesized cotton fabric ion exchangers on a pilot scale. The synthesis is based on grafting of cotton fabrics with (1) glycidyl methacrylate, (2) dimethylaminoethyl methacrylate, and (3) acrylic acid. They then studied characterization of the cotton fabric exchangers (5). Beker et al. synthesized ion exchange resin based on cellulose to remove the heavy metals such as iron, cobalt, copper, and zinc from their aqueous solution (6). Gupta et al. obtained cellulose imino diacetic acid cation exchange resin. They determined cation exchange capacity of this resin to be $3\,\mathrm{meq}\cdot\mathrm{g}^{-1}$ on a dry basis (7). Kim and Kuga prepared a new cellulose-based anion exchanger by grafting polyallylamine onto cellulose (8).

In this study, cellulose ion exchanger was prepared by esterification of hydroxyethyl cellulose with 1,2,3-propanetricarboxylic acid. Ion exchanger characteristics such as swelling percentage, chemical stability, and ion exchange capacities were determined. This resin has some important advantages over the other resin in the literature like high total ion exchange capacity, easy synthesis, lower cost, and simple regeneration.

EXPERIMENTAL

Chemicals

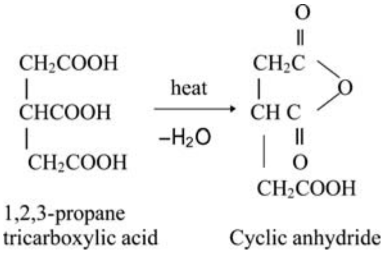
All chemicals used were of analytical reagent grade and at least 99.5% pure. All chemicals were provided by Merck (Darmstadt, Germany). Distilled water was used to prepare the solutions.

Equipment

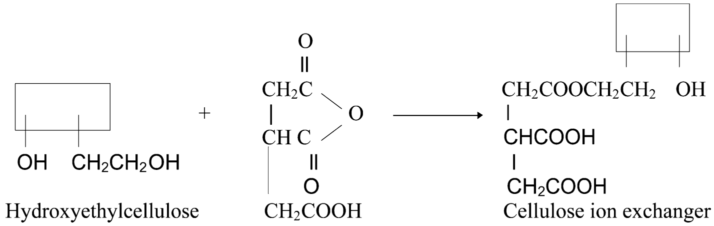
Glass column (30 cm × 1.2 cm I.D.) fitted with fritted glass disks at the bottom was used. The gradient elution apparatus was designed as in previous work (9). The ICP measurements were made on a Varian QEC1401 (Australia). The pH was measured with a Jenway pH meter, model 3040.

Synthesis of the Cellulose Ion Exchanger

The esterification of hydroxyethylcellulose by 1,2,3-propanetricarboxylic acid was performed in two steps: The formation of a cyclic anhydride intermediate by the dehydration of two carboxyl groups and the reaction between hydroxyethylcellulose and the anhydride intermediate to form an ester. Cyclic anhydride intermediate was prepared by heating 1,2,3-propanetricarboxylic acid for 1–2 h at 200°C (Scheme 1). Then, 5.85 g of hydroxyethylcellulose, 20 mL of chloroform, and 5 mL of pyridine were placed into a flask and stirred for 30 min at room temperature. After adding 5.85 g of cyclic anhydride intermediate, the reaction was continued at 50°C for 5 h (Scheme 2). The reaction product was filtered and washed with water and dried at 30°C in vacuo. The yield of the portion obtained by this way was determined as 95% based on total amount of reactants.



Scheme 1.



Scheme 2.

Procedures for Determining Structural and Ion Exchanger Characteristics

In order to determine the chemical structure of the synthesized resin, the degree of substitution, acid and hydroxyl values were determined. The ester value was calculated by means of acid value and degree of substitution.

A 0.5 g of synthesized resin was weighed and transferred to a 100 mL flask. A total of 20 mL of a 0.5 N ethanolic KOH solution was added into the flask. Another flask with the reagent only was prepared as a blank to standardize the alkali. The flasks were stoppered and set aside for 4 h at no higher than 30°C. The solutions were titrated with 0.5 N HCl solution, using phenolphthalein as an indicator. The result was calculated by using the following equation:

$$\text{Degree of substitution: } 56.1.N.(V_2 - V_1)/w$$

where N is normality of HCl, V_1 is volume (in mL) of HCl used in test, V_2 is volume (in mL) of HCl used in blank, and w is weight (in g) of resin.

A 0.5 g of the resin was dissolved in 50 mL of toluene/ethanol (1 : 1) mixture. The solution was titrated with 0.1 N KOH solution, using phenolphthalein as indicator. Acid value was calculated as follows:

$$\text{Acid Value} = 56.1.N.V/w$$

where N is normality of KOH, V is volume (in mL) of KOH used, and w is weight (in g) of resin. A 1 g of the resin was weighted and transferred to a 100 mL flask. A total of 10 mL of pyridine/acetic anhydride (3 : 1) mixture was added into the flask. Another flask with the reagent only was prepared as a blank. The mixtures were kept at 95–100°C in the oil bath for 2 h. After cooling, 1 mL of water was added to the flasks. The flasks were placed again to the oil bath for 15 min. After cooling to room temperature, 10 mL of ethanol was added to the flasks. The solutions were titrated with 0.5 N KOH solution, using phenolphthalein as indicator. Hydroxyl value was calculated as follows:

$$\text{Hydroxyl Value} = 56.1.N.(V_2 - V_1)/w + \text{Acid Value}$$

where N is normality of KOH, V_1 is volume (in mL) of KOH used in test, V_2 is volume (in mL) of KOH used in blank, and w is weight (in g) of resin.

The ester value is the difference between the degree of substitution and the acid value (10).

The swelling percentage measurement was made by allowing the sample of the resin to equilibrate in distilled water overnight under static conditions. The wet weight samples were taken as M_w and the corresponding dry weight as M_d, which was obtained after drying the samples at 100°C until a constant weight. The gravimetric percentage of swelling, α, was calculated as follows:

$$\alpha = \frac{M_w - M_d}{M_d} \times 100$$

The portion (2 g) of resin was kept in water overnight and then transferred to the column. A total of 2 M HCl (100 mL) was passed through the column. It was transferred to a glass stoppered flask. 100 mL of 0.1 N NaOH was added. The flask was shaken for 24 h with a mechanical shaker at room temperature. A total of 50 mL of this solution was put into an Erlenmeyer flask and was titrated with 0.1 N HCl using phenolphthalein. Total ion exchange capacity is defined by

$$C_w = \frac{(100 \times 0.1) - (V \times 0.1 \times 2)}{w}$$

where C_w is total ion exchange capacity as wet, V is volume (in mL) of HCl solution consumed in the titration, and w is amount of resin.

Total ion exchange capacity as dry was calculated as follows:

$$C_d = \frac{C_w}{1 - \alpha/100}$$

where C_d is total ion exchange capacity as dry (11).

Determination of the Acid Dissociation Constants of the Used Resin

A 0.5 g of the resin was weighed and transferred to a 250 mL flask. A total of 20 mL of a 0.5 N ethanolic KOH solution was added into the flask. The mixture was titrated potentiometrically with 0.5 N HCl solution. In each addition (1 mL), the pH electrode of the pH meter was dipped into the aqueous phase and pH values were measured soon after each addition of the titer. Variation of the pH, as a function of mL of the HCl solution added, was pictured (Fig. 1). From the titration curve, dissociation constants of the used ion exchanger were estimated.

Preparation of the Eluting Agent and the Samples Solutions

Sodium trimetaphosphate was used as the elution agent. Firstly, anhydrous sodium trimetaphosphate was prepared from sodium polyphosphate (12), then $Na_3P_3O_9 \cdot 6H_2O$ was prepared from the anhydrous salt (13).

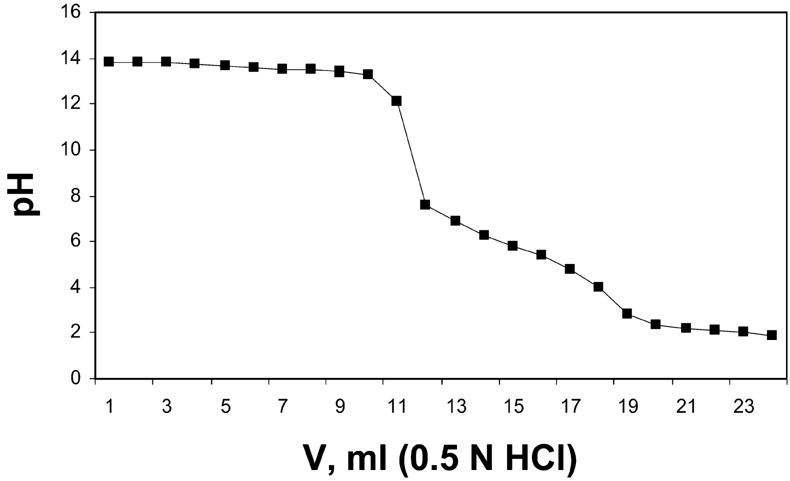


Figure 1. pH-titration curve of the used ion exchanger.

The sample solutions were mainly prepared from the nitrates (Ni, Cr, Co, Fe), the acetates (Pb, Cu, Cd, Zn) of the elements. All compounds were dissolved in water.

PROCEDURE

Distribution Coefficients

The resin was conditioned to the hydrogen form by passing 2 M HCl, 2 M NaCl, and 2 M HCl, respectively, through the resin column. Each time the resin was washed by passing distilled water through the resin, and finally it was dried in air.

The portion (0.5 g) of resin (conditioned to the hydrogen form and its mass corrected by being oven dried at 105°C) was equilibrated in a glass column with sodium trimetaphosphate solution at the desired concentration. It was transferred into a glass stoppered flask. Then 50 mL of the eluent with a known concentration and containing 0.82 meq of the cation of the element to be investigated was added. The flask was shaken by a mechanical shaking device for 15 h at room temperature.

ICP measurements were carried out before and after equilibrium in the solution. The distribution coefficient, K_d, is calculated by the following equation:

$$K_d = \frac{\text{Amount of component in exchanger phase}}{\text{Amount of component in liquid phase}} \times \frac{\text{mL of solution}}{\text{g of dry resin}}$$

Effect of pH

The experiments carried out for the determination of distribution coefficients were repeated at different pH values. The pH was adjusted by adding small aliquots of 6 M hydrochloric acid or sodium hydroxide solutions.

Identification

The elements in the eluted fractions, the qualitative and quantitative determinations of individual heavy metals, were defined by ICP.

Elutions

The resin synthesized was washed several times with distilled water for removal of fine particles. The washed resin was transferred to the column in a water slurry after it was kept in water overnight. Then, approximately 5 mL solution of synthetic mixture which contained 18.75 mg of each element was prepared. The sample, as an aqueous solution, was added to the glass column containing a resin bed 25.5 cm in length which was equilibrated by passing about 250 mL of $5 \cdot 10^{-3}$ M sodium trimetaphosphate solution through it and its top previously rinsed with a small amount of water.

The elements were eluted using $5 \cdot 10^{-3}$ M sodium trimetaphosphate with a flow rate $2\,\mathrm{mL} \cdot \mathrm{min}^{-1}$. Fractions of 5 mL volume were collected.

Another elution was performed for better distribution of peaks. The same amount of sample was taken again. In the first part of this elution, $5 \cdot 10^{-3}$ M sodium trimetaphosphate was used. After 30 mL effluent was taken, the elution was performed using a concentration gradient of $3 \cdot 10^{-3} - 5 \cdot 10^{-3}$ M sodium trimetaphosphate. After 60 mL effluent was taken, $5 \cdot 10^{-3}$ M sodium trimetaphosphate was used again.

Regeneration of the Used Resin

Regeneration of the used resin was performed simply by passing 2 N HCl through the column until converting to hydrogen form and was washed with distilled water until the pH of the wash water was 7.0.

RESULTS AND DISCUSSION

Some chemical and physical characteristics of the synthesized resin are given in Table 1.

Table 1. Some chemical and physical characteristics of the synthesized resin

Polymer matrix structure	Ethyl cellulose
Functional groups	$-COOH$
Physical form and appearance	Powdered, beige
Ionic form	Hydrogen
Moisture retention	19.8 %
Particle size	40–80 μm
Surface area	$200\,m^2 \cdot g^{-1}$
Packing density	$0.5\,g \cdot mL^{-1}$
Acid value	78.5
Hydroxyl value	178.2
Degree of substitution	252.4
Ester value	173.9
Total ion exchange capacity, dry	$4.1\,meq \cdot g^{-1}$
Total ion exchange capacity, wet	$3.3\,meq \cdot g^{-1}$

The dissociation constants of the used ion exchanger were calculated from the titration curve in Fig. 1. The dissociation constant values were found to be $\log K_{d1} = 13.6$ and $\log K_{d2} = 5.8$.

The experimental distribution coefficients are presented in Table 2. As can be seen from this table, there are enough differences between the distribution coefficients for the separations of the elements except in case of $3 \cdot 10^{-3}$ M. For separations $5 \cdot 10^{-3}$ M sodium trimetaphosphate is very convenient and $3 \cdot 10^{-3}$ M sodium trimetaphosphate can be used for gradient elutions in order to minimize the elution times.

The effect of pH on the ion exchange capacity is summarized in Table 3. As can be seen from the table, the exchange capacity reaches a maximum

Table 2. Distribution coefficients in different concentrations of sodium trimetaphosphate solutions

	Concentration of sodium trimetaphosphate				
Heavy metals	$3 \cdot 10^{-3}$ M	$5 \cdot 10^{-3}$ M	0.01 M	0.05 M	0.1 M
Cr	1.2	2.3	8.9	18.3	25.7
Ni	3.2	5.3	12.4	21.7	26.6
Co	4.3	6.9	17.1	24.8	29.4
Cd	5.4	9.4	17.6	27.4	29.9
Zn	6.0	10.1	26.4	27.8	29.9
Fe	7.9	12.8	26.6	29.7	33.7
Cu	9.2	14.0	28.7	33.5	37.8
Pb	11.4	16.8	32.8	36.6	41.4

Table 3. The effect of pH on the ion exchange capacity

	The amount of metal captured by resin at different pH values (mmol.100 mL^{-1})			
Heavy metals	2	4	6	8
Cr	0.10	0.11	0.79	0.78
Ni	0.10	0.10	0.80	0.79
Co	0.10	0.10	0.81	0.79
Cd	0.12	0.12	0.81	0.79
Zn	0.10	0.11	0.81	0.79
Fe	0.10	0.10	0.81	0.80
Cu	0.11	0.11	0.81	0.79
Pb	0.09	0.09	0.81	0.79

value at pH 6. At lower pH values, the exchange capacity is decreased. On the other hand, at higher pH values, alkali metal becomes competitive to heavy metal ions and prevents the binding of heavy metal to resin matrix.

First elution curves are shown in Fig. 2. As can be seen from the figure, all elements were eluted within 260 mL effluent being collected, and they were separated completely from each other.

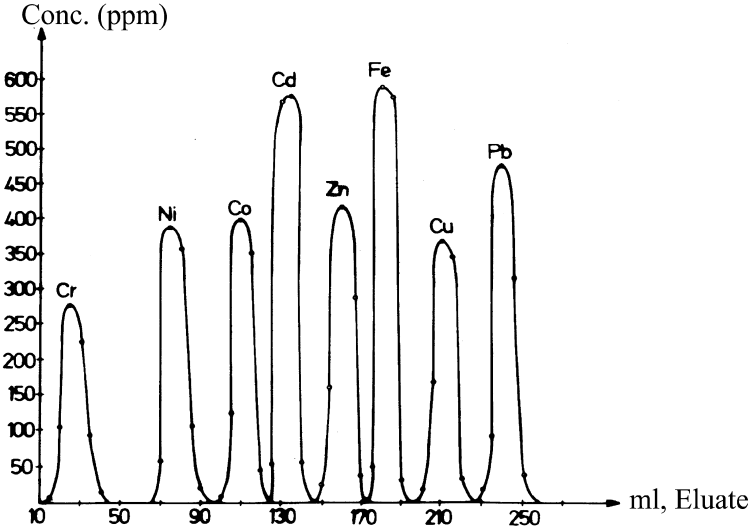


Figure 2. Elution curves of the elements (18.75 mg of each) with 5 · 10^{-3} M sodium trimetaphosphate; resin bed 25.5 cm × 1.2 cm, flow rate 2 mL · min^{-1}; IEC: 3.3 meq · g^{-1} (wet); 4.1 meq · g^{-1} (dry); swelling percentage: 19.8 %; average separation percent: 99.4 %.

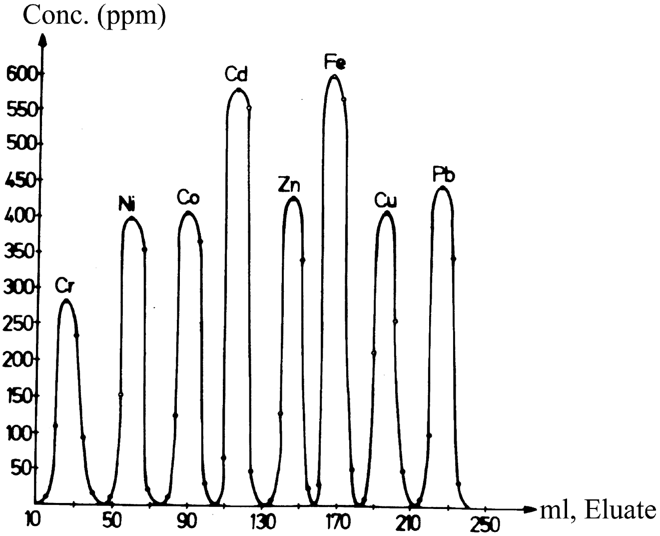


Figure 3. Elution curves of the elements (18.75 mg of each) with first, 30 mL $5 \cdot 10^{-3}$ M sodium trimetaphosphate and with 30 mL $3 \cdot 10^{-3}$–$5 \cdot 10^{-3}$ M concentration gradient of sodium trimetaphosphate and then with $5 \cdot 10^{-3}$ M sodium trimetaphosphate; resin bed 25.5 cm × 1.2 cm, flow rate 2 mL · min^{-1}; IEC: 3.3 meq · g^{-1} (wet); 4.1 meq · g^{-1} (dry); swelling percentage: 19.8 %; average separation percent: 99.4 %.

Second elution curves are represented in Fig. 3. This elution was completed in 240 mL of eluent at a flow rate of 2 mL · min^{-1}. The separations were carried out very well.

The qualitative and quantitative determinations of individual elements in the fractions were defined by ICP. Results of quantitative analysis are shown in Table 4.

Table 4. Results of quantitative analysis

First elution		Second elution	
Element	Separation percent	Element	Separation percent
Cr	97.1	Cr	96.9
Ni	99.4	Ni	99.0
Co	99.8	Co	99.7
Cd	99.8	Cd	99.7
Zn	99.8	Zn	99.9
Fe	99.8	Fe	100.0
Cu	99.8	Cu	99.9
Pb	99.9	Pb	99.8

CONCLUSION

In this study, the prepared resin can be simply made and the cost is low. The capacity was determined as $4.1\,\mathrm{meq} \cdot \mathrm{g}^{-1}$ resin, and this value is high compared to others given in the literature. This resin has a large surface area, which makes the adsorption rate of the heavy metals rapid. The regeneration of resin is very simple. Furthermore, it has been demonstrated that sodium trimetaphosphate is a very suitable elution agent for the separation of heavy metals on this resin. By using a concentration gradient of elution very good separations were obtained. In these elutions, very low concentrations of sodium trimetaphosphate were used. As a result, the resin synthesized can be used as an adsorbent for the effective removal of Pb, Cd, Co, Cu, Fe, Ni, Zn, and Cr from aqueous solutions.

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