

Synthesis and Characterization of Cellulose Ion Exchanger. II. Pilot Scale and Utilization in Dye–Heavy Metal Removal

A. WALY, F. A. ABDEL-MOHDY, A. S. ALY, A. HEBEISH

National Research Centre, Textile Research Division, Dokki, Cairo, Egypt

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ABSTRACT: Cotton fabric was converted into an ion exchanger by grafting it with (1) glycidyl methacrylate (GMA), followed by aminization with ethylene diamine; (2) dimethylaminoethyl methacrylate (DMAEMA), followed by quaternization; and (3) acrylic acid (AA). Grafting was carried out on a pilot scale using a thiocarbonate–H₂O₂ redox system. The so-obtained cotton graft copolymers were monitored for their ability to remove different dyes as well as heavy metals from aqueous solutions. It was found that the magnitude of dye exhaustion was as follows. For direct and reactive dyes the percentage of exhaustion follows the order of aminized GMA > quaternarized DMAEMA > DMAEMA, whereas for acid dye the percentage of exhaustion follows the order of quaternarized DMAEMA > DMAEMA > aminized GMA. On the other hand poly(AA)–cotton copolymer is very effective at removal of the basic dye. With respect to heavy metal ions removal, the copolymers show the following order: AA > aminized GMA > quaternarized DMAEMA > DMAEMA. While dichromate removal follows the order of quaternarized DMAEMA > DMAEMA > aminized GMA. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 2151–2157, 1998

Key words: cellulose; ion exchanger; dye; heavy metal

INTRODUCTION

Recently, a number of studies have been reported with regard to the adsorption and dye removal processes using various adsorbents.¹ A novel series of cation–anion exchange starches have been prepared and evaluated.² Previous reports have also dealt with preparation of cation exchange starches containing phosphoric acid groups³ and carboxyl groups.⁴ Anion exchange starches containing amino groups were prepared and characterized.⁵ Moreover, preparation and technological evaluation of starch-bearing aromatic groups were reported.⁶ Similarly, anion-exchange celluloses were prepared and characterized with emphasis on their capacity.⁷

This work is undertaken with a view to prepare cotton fabric ion exchangers on a pilot scale. The preparation is based on grafting of cotton fabrics with (1) glycidyl methacrylate (GMA) followed by aminization with ethylene diamine, (2) dimethylaminoethyl methacrylate (DMAEMA) followed by quaternization, and (3) acrylic acid (AA). Characterization of the cotton fabric exchangers so obtained are studied.

EXPERIMENTAL

Materials

Cotton fabric (400 g/m²; 21 picks × 61 ends/cm) was supplied by Misr Spinning and Weaving Co., Mehalla El-Kubra. Cotton fabric was used after purification by scouring for 2 h at the boil using aqueous solution containing 1% sodium hydrox-

Correspondence to: A. Hebeish.

ide. It was then thoroughly washed and air-dried at room temperature.

GMA and DMAEMA (Aceto Corporation, New York), were commercial grade chemicals distilled before use. Potassium dichromate, copper acetate, and cobalt acetate (Fluka, Switzerland) were pure chemicals. Sodium hydroxide and ferrous sulfate (ADWIC, Egypt) were also pure grade chemicals. Carbon disulfide (ESCO, Egypt), AA (Merk, Germany), and ethylene diamine [s.d. fine chemical Ltd., POICHIA (R)] were chemicals for synthesis.

Thiocarbonation of Cotton Fabric

The cotton fabric sample was treated in a "jigger" (semi-pilot machine used for continuous dyeing and finishing of textile fabrics) containing the thiocarbonation solution (1% NaOH (w/v), 2% CS₂ (v/v), and a suitable wetting agent to increase the efficiency of the thiocarbonation reaction. The material-to-liquor ratio was 1 : 20, and the sample was in continuous movement in the thiocarbonation solution at 30°C to ensure complete homogeneous treatment for the sample. After 1 h, the solution was drained, and the sample was thoroughly washed with cold distilled water until the washing liquor acquired pH 7.

Grafting Procedure

The cotton thiocarbonate sample was pretreated in a jigger containing aqueous solution of 0.1% ferrous sulfate for 30 m at 30°C with continuous movement to avoid the heterogeneous deposition on the sample surface. The sample was washed thoroughly with distilled water.

The sample was placed in a jigger containing the following polymerization solution: H₂O₂ (0.2%) and the monomer (100% w/w sample). The polymerization was carried out at pH 2 and 30°C for 2 h using a material-to-liquor ratio of 1 : 20. The sample was under continuous movement during the polymerization reaction. After the 2 h of polymerization, the solution was drained, and the sample was thoroughly washed with distilled water and repeatedly extracted with a proper solvent.

Quaternization of Poly(DMAEMA)–Cotton Copolymer

Samples of poly(DMAEMA)–cotton copolymer were pretreated with 8% aqueous NaOH solution

and then padded in pure epichlorohydrin. The reaction was carried out in the jigger for 2 h at 60°C.⁸

Aminization of Poly(GMA)–Cotton Fabric Copolymer

The poly(GMA)–cotton copolymer sample was treated with ethylene diamine at 80°C for 3 h using the jigger with continuous movement. The sample was then thoroughly washed with distilled water and dried at 50°C for 24 h before analysis.^{9,10}

Regeneration of the Exchanger

The cotton fabric exchangers were treated with 0.5N HCl and 0.5N NaOH, respectively, for 2 h each and then washed with twice-distilled water until pH 7. The test for the exhaustion was done for a second time.

Analysis and Test Methods

The percentage of polymer add-on was calculated as follows:

$$\text{Polymer add-on\%} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 is the dry weight of original sample, and W_2 is the dry weight of grafted sample.

The extent of grafting with DMAEMA and aminization of poly(GMA)–cotton fabric copolymer was monitored through nitrogen content (N%) using the Kjeldahl method.¹¹

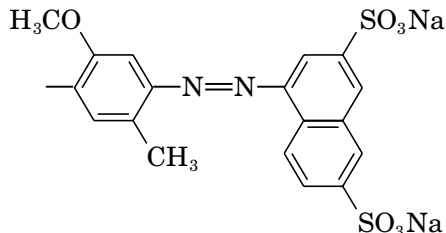
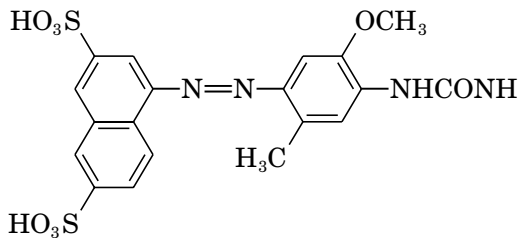
Estimation of free epoxy rings in poly(GMA)–cotton copolymer was based on methods described elsewhere.^{12,13}

The carboxyl content was determined as described in Daul et al.¹⁴

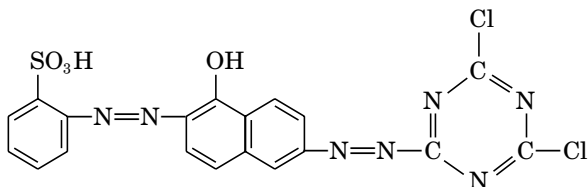
The total ion-exchange capacity was determined by the method reported by Kunin.¹⁵

Exhaustion of Dyes

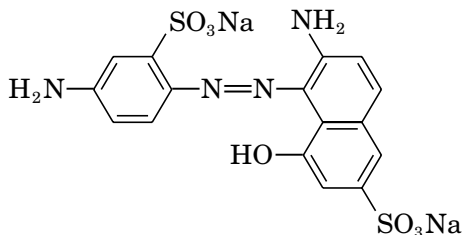
The dyes used in the adsorption experiments are shown below and were used as in the following commercial form:



where direct dye is chlorantine fast red 6 BLL (C.I. 29065, λ_{\max} 490)



where reactive dye is procion brilliant orange MG (C.I. 17907, λ_{\max} 479)



where acid dye is erio-vilot R 170 (C.I. 170, λ_{\max} 580) and where basic dye is maxilon red BL-N (λ_{\max} 530).

The structure of this dye is not available in the color index.

Solutions (100 mL) containing different dyes were independently applied to the cotton fabric ion exchangers (2 g). After 24-h contact time, the samples were raised from the solutions.

Measurement of the percentage of dye exhaustion was determined using Photoelectric Colorimeter Model 581.

Heavy Metal Ions Removal

Two grams of ion exchanger sample was introduced into a container containing 100 mL of cation

salt solution (2.5 g/L) and left for 24 h. The sample was then filtered, and the concentration of cations in the original solution and the filtrate were determined by 2 ARGELY EDTA titration.¹⁶

$$\text{Exhaustion \%} = \frac{X - X'}{X} \times 100$$

where X and X' are the concentration of the cations before and after treatment with the samples.

Removal of Dichromate

The stock solution of $\text{Cr}_2\text{O}_7^{2-}$ was prepared by dissolving 250 mg $\text{K}_2\text{Cr}_2\text{O}_7$ in 1 L of twice-distilled water. 2 g of grafted sample were treated with a solution containing 25 mg $\text{K}_2\text{Cr}_2\text{O}_7$. After 24 h of contact time, the solution was filtered, and the residual dichromate concentration in the filtrate was measured against thiosulfate solution.¹⁷

Exhaustion of the dichromate was calculated as follows:

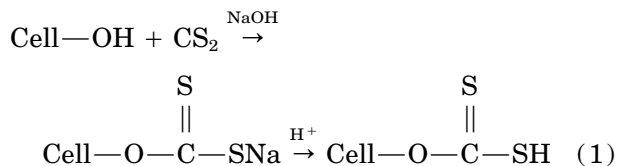
$$\text{Exhaustion \%} = \frac{X - X'}{100} \times 100$$

where X is the dichromate concentration (meq/100 g) before treatment, and X' is the dichromate concentration (meq/100 g) after treatment.

RESULTS AND DISCUSSION

Tentative Mechanism

Cellulose reacts with carbon disulphide to yield cellulose thiocarbonate, as shown by the mechanism suggested by eq. (1), as follows:



Disintegration of the thiocarbonate groups and/or its involvement in a redox reaction with an oxidant lead ultimately to cellulose macroradical, as shown in eq. (2), as follows:

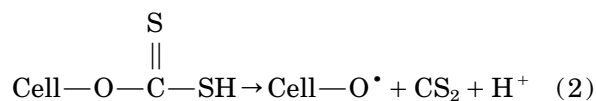


Table I The Analysis Results of Poly(GMA, DMAEMA, and AA)–Cellulose Graft Copolymers

Properties	Exchanger I	Exchanger II	Exchanger III
Polymer add on (%)	25	21	50
Initial epoxy content (m eq/100 g)	126		
Nitrogen content (N%)	1.93	1.19	
Acidity value (mmol/100 g)	9.2	85	
Carboxylic content (meq/100 g)			375
Ion exchange capacity (mmol/100 g sample)	173	108	460

Exchanger I, aminized poly(GMA)–cotton copolymer; exchanger II, quaternized poly(DMAEMA)–cotton copolymer; exchanger III, poly(AA)–cotton copolymer.

changer based on poly(AA)–cotton copolymer exhibits the highest ion exchange capacity, whereas quaternized poly(DMAEMA)–cotton copolymer exhibits the least. On the other hand, aminized poly(GMA)–cotton copolymer stands in the mid-way position. The significant differences among the three exchangers with respect to the percentage of polymer add-on account for such diversity in capacity. Indeed, the capacity is directly related to the percentage of polymer add-on.

Removal of Dyes

Table II shows the ability to remove dyes of different ion exchangers, namely, aminized poly(GMA)–cotton copolymer (exchanger I), quaternized poly(DMAEMA)–cotton copolymer (exchanger II), and poly(DMAEMA)–cotton copolymer (exchanger IV). Dyes used encompass direct, reactive, and acid dyes. The results signify the three following main features.

1. The three exchangers under investigation are

capable of partial dye removal, irrespective of the nature of the dye.

2. The extent of dye removal is determined by nature of both the exchanger and the dye.
3. The ability of the exchanger to remove the dye decreases after regeneration.

Hence, the extent of direct dye removal, as evidenced by the results of dye exhaustion, brings up the following order: exchanger I > exchanger II > exchanger IV. The capacity of the ion exchanger to hold the direct dye is a manifestation of the ability of the amino and hydroxyl groups of the exchanger, along with the pore size of its physical structure.

Table II also shows that the acid dye can be successfully adsorbed with the ion exchangers in question. The extent of acid dye removal follows the order of exchanger II > exchanger IV > exchanger I. This order implies that quaternized poly(DMAEMA) and poly(DMAEMA)–cotton copolymers exhibit larger capacities for acid dye removal than the aminized poly(GMA)–cotton co-

Table II Ability of Different Ion Exchangers to Remove Dyestuffs of Various Nature

Ion Exchanger	Exhaustion (%)					
	Direct Dye		Reactive Dye		Acid Dye	
	A	B	A	B	A	B
Poly(DMAEMA)–cotton copolymer (exchanger IV)	40.8	37	74	51	85	65
Quaternized poly(DMAEMA) cotton copolymer (exchanger II)	55	42	85	63	99.6	82
Aminized poly(GMA)–cotton copolymer (exchanger I)	87	65	96	80	55	40

A, first time treatment before regeneration; B, second time treatment after regeneration.

Table III Ability of Poly(AA)–Cotton Copolymer to Remove Basic Dye and Cu²⁺ and Co²⁺ Ions from Aqueous Solutions

Ion Exchanger	Dye Exhaustion (%)		Heavy Metal Ion Removal (%)			
	Basic Dye		Cu ²⁺		Co ²⁺	
	A	B	A	B	A	B
Poly(AA)–cotton copolymer	99.8	75	100	100	100	100

A, before regeneration; B, after regeneration.

polymer. This seems to be in agreement with the basicity of the copolymer: the higher the basicity, the greater the interaction with the acid dye. It is understandable that the basicity of the amino groups containing exchanger is greatest with the tertiary amine and least with the primary amine.

With reactive dyes, on the other hand, the extent of dye removal categorized the exchangers under investigation according to the following order (Table II): exchanger I > exchanger II > exchanger IV. Here, the interactions of the dye with the exchanger stem from the hydroxyl and amino groups of the copolymer. While the cellulose hydroxyls of the copolymer act as sites for dye sorption, they also act as reactive centers for reaction of the dye under the influence of the amino groups, which act as a built-in catalysts. Meanwhile, the amino groups themselves interact with the dye via formation of salt linkage.

Dependence of the extent of dye removal upon the nature of the dye (Table II) is rather expected. The nature of the dye (molecular size, functional groups and other substituents, configuration, etc.) is expected to decide the affinity of the dye for the exchanger, which, in turn, is governed by as many factors as penetration, availability, and selectivity accessibility.

It is further noted that, irrespective of the nature of the dye and the nature of the exchanger, the capacity of the latter decreases after regeneration. This state of affairs indicates that the use of the exchanger in the first dye treatment detract from its ion exchange properties. Most probably, some of the functioning groups are either blocked or removed during the regeneration process.

Table III shows the attractive results of poly(AA)–cotton copolymer (exchanger III) as an adsorbent of basic dye; the dye exhaustion attains values of 99.8 and 75% before and after regeneration, respectively. It is understandable that exchanger III functions mainly through its carboxyl

groups. Removal of the basic dye by this particular exchanger occurs via ionic forces holding the dye molecules to the exchanger. The decrement in the ability of the latter to remove the dye after regeneration suggests partial disappearance of the carboxyl groups of the exchanger and/or their blocking with some dye molecules, which are difficult to get rid of during the regeneration process. Indeed, the outstanding effectiveness of exchanger III in removing the Cu²⁺ and Co²⁺ ions, which reaches 100% or complete removal before and after regeneration, substantiates the latter possibility. That is, some of the carboxyl groups of the copolymer are partially blocked by the basic dye, and such blocking is responsible for the decrement in ability of exchanger III after regeneration to remove the basic dye.

Removal of Metal Ions

Returning to Table III, it is clear that exchanger III, which refers to poly(AA)–cotton copolymer, offers an excellent means for Cu²⁺ and Co²⁺ ions from aqueous solutions. 100% removal of these ions could be achieved by exchanger III before and after being subjected to the regeneration process. This is not the case with the other exchangers (Table IV). The percentage of Cu²⁺ and Co²⁺ ions removal lies between 3–6% for exchanger II and exchanger IV, while it goes up to 54 and 40% for exchanger I in the case of Cu²⁺ and Co²⁺ ions, respectively. Absence of the cationic properties, particularly in exchanger II and exchanger IV, accounts for this.

A different situation is encountered for removal of dichromate ions (Table IV). The highest dichromate removal is observed with exchanger II and the least with exchanger I. Exchanger IV lies in between. This reflects differences in the anionic characteristics among these three exchangers.

Table IV Dependence of Heavy Metal Ions Removal on Nature of the Exchanger

Ion Exchange	Removal (%)				Cr ₂ O ₇ ²⁻
	Cu ²⁺		Co ²⁺		
	A	B	A	B	
Poly(DMAEMA)– cotton copolymer (exchanger IV)	5	—	3	—	76
Quaternarized poly(DMAEMA)– cotton copolymer (exchanger II)	6	—	5	—	80
Aminized poly(GMA)– cotton copolymer (exchanger I)	54	53	40	39	55

A, before regeneration; B, after regeneration.

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