Chemical modification of linen fabrics for salt free dyeing with anionic dyes

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REZUMAT – ABSTRACT

Modificarea chimică a țesăturilor de in pentru vopsirea fără săruri cu coloranți anionici

După cum bine se cunoaște, pentru a reduce forțele de respingere ionică între fibrele celulozice având încărcătură anionică în baia de vopsire și coloranții anionici (direcți, reactivi etc.) utilizați în vopsire, este necesar să se adauge o cantitate considerabilă de sare în baia de vopsire, în special în timpul vopsirii cu coloranți reactivi. Salinitatea ridicată din apele reziduale reprezintă un pericol pentru mediu. Din acest motiv, în acest studiu, țesăturile de in au fost supuse procesului de cationizare pentru a realiza vopsirea fără săruri cu coloranți direcți și reactivi. Pentru a determina condițiile optime ale procesului de cationizare, țesăturile de in au fost tratate cu agent de cationizare pe bază de amoniu cuaternar cu poliamino-clorhidrină la diferite concentrații, valori ale pH-ului, timpi și temperaturi. Tesăturile cationizate au fost vopsite cu coloranți direcți și reactivi. Conținutul de azot (N%), analizele în infraroșu cu transformata Fourier (FTIR) și microscopia electronică de scanare (SEM) au fost, de asemenea, realizate pentru a investiga efectele procesului de cationizare asupra structurii chimice și morfologice a fibrelor de in. Conform rezultatelor experimentale, condițiile optime pentru cationizarea țesăturilor de in sunt: 9% agent de cationizare, pH 10 și 75°C timp de 45 de minute. Mai mult, s-a stabilit că eficiența culorii a fost mai mare în cazul țesăturilor de in cationizate și vopsite fără săruri, comparativ cu probele netratate și vopsite convențional.

Cuvinte-cheie: in, cationizare, vopsire fără săruri, eficiența culorii, colorant direct, colorant reactiv

Chemical modification of linen fabrics for salt free dyeing with anionic dyes

As is known, in order to reduce the ionic repulsion forces between cellulosic fibers having anionic charge in the dyebath and anionic dyestuffs (direct, reactive, etc.) used in dyeing, it is necessary to add a considerable amount of salt to the dyebath particularly during reactive dyeing. The high salinity in the wastewater is an environmental hazard. For this reason, in this study linen fabrics were subjected to cationization process in order to achieve salt free dyeing with direct and reactive dyes. In order to determine the optimum conditions of cationization process, linen fabrics were treated with polyaminochlorohydrin quaternary ammonium based cationization agent at different concentrations, pH values, times and temperatures. Then the cationized fabrics were dyed with direct and reactive dyes. Nitrogen content (N%), Fourier transform infrared (FTIR) and scanning electron microscopy (SEM) analyses were also realized to investigate the effects of cationization process on chemical and morphological structure of flax fibers. According to the experimental results, the optimum conditions for cationization of linen fabrics were found to be 9% cationization agent, pH 10 and 75°C for 45 minutes. Furthermore, it was determined that the color efficiency was higher in case of cationized and salt free dyed linen fabrics compared to the un-treated and conventionally dyed samples.

Key words: Linen; cationization; salt free dyeing; color efficiency; direct dye; reactive dye

INTRODUCTION

Flax is a multicellular, lustrous and very compact bast fiber with a high stiffness and excellent tensile properties [1]. Flax (*Linum usitatissimum L.*) is obtained from the stem of plants belonging to the family *Linacea* [2]. On the other hand, linen is the yarn or the fabric made from flax fibers [3]. The main chemical constituents of flax fibers are α-cellulose, hemicellulose, lignin, pectin along with a small amount of fats, waxes, nitrogenous compounds, residual ash and natural coloring matter [4]. As compared with cotton, flax fiber has some advantages. It is stronger than cotton and it is better than cotton as a conductor of heat. On the other hand, it is less elastic than cotton and creases easily [5]. Like cotton, linen can be dyed with direct, vat and reactive dyes [6]. When cellulosic fibers come in contact with water, they produce slightly negative charge due to the ionization of hydroxyl groups. This slightly negative charge on the fiber results in repulsion of anionic dye molecules and for this reason the exhaustion and levelling of dye molecules are affected. However, the ionic repulsion factor can be offset by adding an electrolyte and hence increased dye exhaustion can be achieved [7]. In current practice, reactive dyes are predominantly used for dyeing of cotton due to their high wet fastness properties, brilliant colors and wide range of hue. However, most of the commercially available reactive dyes show low affinity to cotton, so high concentrations of sodium chloride or sodium sulfate salts (30–100 g/L) are required in the dyebath to enhance dye-fiber interactions. The need of high amounts of salt usage leads to serious environmental pollution [8]. It increases salinity of the rivers and this affects the delicate biochemistry of aquatic life [9]. For this reason over the years a number of studies on the finishing of cotton fibers have been carried out to improve their dye-uptake properties. The focus of most research was to provide cationic sites on these

fibers for increasing their interaction with anionic dyes [10].
Many scientists have been working for a long time to increase the cotton fiber's substantivity to anionic dyes via applying pre-treatment to fiber with cationic substances [11]. In most of these studies, quaternary cationic agents which contain various reactive groups (epoxy, active halogen, ethoxylate or amino) were used [12]. With the use of epoxyamine or quaternary epoxyammonium compound, a cationic site can be introduced in cellulose through reaction of an epoxy radical in alkaline medium and, therefore, the reactivity of cellulose towards anionic dyes is modified [7]. Reviewing the literature, it can be understood that most of the studies were carried out on cotton fibers [for example: 13–20] and studies on flax fiber are limited. Although one can comment that results of these studies can be applied to linen fabric due to having identical chemical composition with cotton, flax fiber in linen fabric has different molecular and morphological structure which will largely determine the degree of modification. Therefore, modifications carried out on cotton fabric cannot be directly applied to linen fabric [21]. For this reason it is also needed to be realized some studies on linen fabrics.
Hebeish et al. investigated the factors affecting the cationization reaction with Quat-188 (3-chloro-2-hydroxypropyltrimethyl ammonium chloride) of linen fabric both for the exhaustion and the cold pad-batch methods [21]. In another study, they cationized linen fabrics by using 3-chloro-2-hydroxypropyl trimethyl ammonium chloride in alkaline medium with cold pad-batch method. Then cationized linen fabrics were dyed with reactive, direct and acid dyes in the absence of salt [22].
Mashaly and Hauser cationized the linen fabric through the reaction of two different commercial cationizing agents; 3-chloro-2-hydroxypropyltrimethyl ammonium chloride and polyaminochlorohydrin quaternary ammonium salt with epoxide functionality. Then unmodified and cationized linen fabrics were dyed with four different types of fiber reactive dyes by using the cold pad-batch dyeing method [23]. In another study, they investigated the dyeability of linen fabrics with acid and direct dyes after cationization by using the 3-chloro-2-hydroxypropyltrimethyl ammonium chloride and polyhexamethlene biguanides [24].
In this study linen fabrics were subjected to the cationization process by using polyaminochlorohydrin quaternary ammonium salt with epoxide functionality (commercial name: Albafix E) by exhaustion method. In literature, there is already a cationization process by exhaustion method developed by Hebeish et al. for salt free dyeing of linen fabrics with reactive dyes. In that study, Quat-188 had been used as a cationization agent and dyeability of cationized linen fabrics had been investigated for only reactive dyes [21]. On the other hand, in this study chemical modification of linen fabrics was carried out with another cationization agent (Albafix E) and change in their dyeability after cationization process was investigated both with direct and reactive dyes. Although Mashaly and Hauser had previously used the same cationization agent in their research, they had determined the optimum conditions of cationization process for cold pad-batch method [24]. But, it will be very useful if a cationization process for linen fabric could be developed by exhaustion method. Because, in this case, it would be possible to carry out both the cationization and dyeing processes on the same equipment.

EXPERIMENTAL WORK

Bleached 100% linen plain woven fabric [24 yarns/inch in warp (Tex 40) and 21 yarns/inch in weft (Tex 40)] with a weight per unit area 510 g/m^2 was used in this study. Solophenyl Red 3BL (C.I. Direct Red 80) and Remazol Blue BB (C.I. Reactive Blue 220) were kindly supplied by Hunstman and Dystar respectively. Cationization agent Albafix E, a polyaminochlorohydrin quaternary ammonium polymer, was provided by Hunstman. The chlorohydrin form of the reagent can be converted to the epoxy form in the presence of alkali [21]. The reaction is shown in figure 1.
This epoxy form has the ability of reacting with cellulose via ether formation as shown in figure 2.

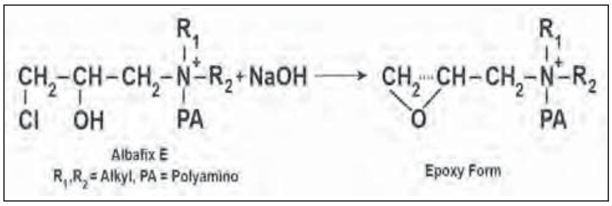

Fig. 1. Chemical structure of Albafix E and its transformation to epoxy form [25]

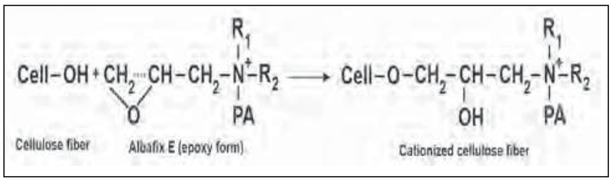

Fig. 2. Reaction between epoxy form of cationization agent (Albafix E) and cellulose

Optimization

Linen fabrics were cationized with Albafix E in a laboratory scale dyeing machine (Termal HT) using exhaustion method. In order to determine the optimum conditions of cationization process, four factors potentially affecting this process were evaluated, namely cationizing agent concentration (3–6–9%), pH (4–7–10), treatment time (15–30–45 min.) and treatment temperature (25–50–75°C). At the end of the treatment, each sample was taken out and washed several times with cold water and dried at ambient conditions. Experiments were carried out according to the orthogonal experimental design. The orthogonal experimental design contains three levels

Table 1

Factor symbol	Factor	1	2	3
X_1	Concentration (%)	3	6	9
X_2	pH	4	7	10
X_3	Time (min.)	15	30	45
X_4	Temperature (°C)	25	50	75

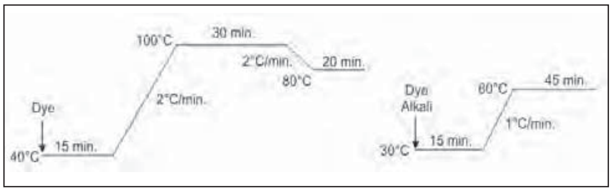

Fig. 3. Dyeing graphs for direct (on the left) and reactive dyes (on the right)

Table 2

Trial no.	Conc. (%)	pH	Time (min.)	Temp. (°C)	$(K/S)_{direct}$	$(K/S)_{reactive}$
1	1	1	1	1	6.49	7.05
2	1	2	2	2	8.88	8.36
3	1	3	3	3	12.52	11.11
4	2	1	2	3	8.57	9.34
5	2	2	3	1	8.64	9.60
6	2	3	1	2	11.23	10.56
7	3	1	3	2	9.67	10.06
8	3	2	1	3	10.19	10.11
9	3	3	2	1	10.35	10.17

for each factor, the coded levels and actual values being shown in table 1.

The pattern of the levels of the each factor is shown in table 2 along with the color yield (K/S) values resulting from the individual trials.

The cationization efficiency of linen fabric was tested by using salt free dyeing. For this aim cationized linen fabrics were dyed with a direct (Solophenyl Red 3BL) and a reactive (Remazol Blue BB) dye without salt usage. After dyeing, color efficiency (K/S) values of the samples were evaluated. Higher K/S indicates higher extent of cationization and vice versa.

Dyeing procedure

After determining the optimum conditions of cationization process, linen fabrics were treated at these conditions and then dyed with a direct and a reactive dye without salt usage. All reactive dyeings were carried out by using 13 g/L soda ash. In the conventional dyeing of un-treated samples 15 g/L and 50 g/L natriumsulphate salt was used for direct and reactive dyes respectively.

All dyeings were carried out in a laboratory scale dyeing machine (Termal HT) at 40:1 liquor ratio. Initial pH of dyeing was 6.5–7. Dyeing graphs for direct and reactive dyes are given in figure 3.

After dyeing with direct dye, samples were rinsed. On the other hand, for reactive dyes washing steps were as follows: cold rinsing (10 min.) → neutralization at 60ºC (with 0.5–1 g/L acetic acid) → rinsing at 80ºC → rinsing at 95ºC (15 min.) → rinsing at 80ºC (10 min.) → cold rinsing. Subsequently color (both K/S and CIE L*a*b* values) and fastness (washing, rubbing and light) properties of these samples were compared with conventionally dyed samples.

– ***Color measurements:*** CIE L*a*b* (L*: lightness (where L* = 100 for the perfect white and L* = 0 for the perfect black), a*: red (+a*) and green (–a*) coordinate, b*: yellow (+b*) and blue (–b*) coordinate) color values and reflectance (%R) values of the dyed samples were determined on X-Rite Color i7 reflectance spectrophotometer with illumination/observer conditions set at D65/10° at the maximum absorption wavelength of each dye (540 and 620 nm for direct and reactive dye respectively). Then the color efficiency (K/S) was calculated from Kubelka-Munk equation as shown below:

$$K/S = (1 - R)^2/2 \cdot R$$

where R is the reflectance of the dyed sample, K – the absorption coefficient and S – the scattering coefficient. For color measurements, 3 samples were tested to compute the average value.

– ***Color fastness tests:*** The color fastnesses to washing, rubbing and light were assessed according to ISO 105-C10 [26], ISO 105-X12 [27], and ISO 105-B02 [28] standard test methods respectively. Washing tests were carried out at 60°C for 30 min. by using 4 g/L ECE standard test detergent.

Determination of the effects of cationization treatment on chemical properties of linen fabrics

In order to explain why dye-uptake of linen fabrics increase after cationization treatment, cationized and un-treated fabric samples were subjected to nitrogen content (N%) and Fourier transform infrared (FTIR) analyses. Scanning electron microscopy (SEM) analyses were also done. On the other hand, whiteness degrees of fabrics were measured to understand better the color nuance difference between un-treated and cationized fabrics dyed at the same conditions.

– ***Nitrogen content (N%) analysis:*** Nitrogen content of the linen fabric before and after cationization, was determined according to Kjeldahl test method by using Gerhardt Kjeldahlterm Vaposdest test device.

– ***Fourier Transform Infrared Spectroscopy (FTIR) analysis:*** Fourier transform infrared (FTIR) spectra of cationized and un-treated samples were recorded over the range 500–4000 cm^{-1} on a Vertex 70 ATR-FTIR Spectrometer, Bruker.

– ***Scanning Electron Microscopy (SEM) analysis:*** In order to examine the surface structure of the cationized flax fibers scanning electron microscopy (SEM) analyses were carried out. For this aim, Quanta FEG 250 scanning electron microscope (FEI, Netherland) was employed for imaging the fabric samples at 5000X and 10000X magnifications with accelerating voltage of 5 kV.

– Whiteness degree measurement: With the aim of determining the effect of cationization process on color of linen fabrics, their whiteness degrees (according to Berger) were measured prior to dyeing with Gretag Macbeth E700 spectrofotometer.

RESULTS AND DISCUSSION

Results related to the optimization of the cationization treatment

In order to determine the optimum conditions of cationization process, linen fabrics were treated with Albafix E at different concentrations (3–6–9%), pH values (4–7–10), times (15–30–45 min.) and temperatures (25–50–75°C). Then cationized fabrics were dyed with a direct and a reactive dye. The color yields (K/S) of the cationized fabrics were taken as a measure of the extent of cationization. Results are given in figure 4 and figure 5.

Results of analysis of variance related to the K/S values of linen fabrics dyed with direct (C.I. Direct Red 80) and reactive (C.I. reactive Blue 220) dye are given in table 3 and table 4 respectively.

Discussions of the results obtained are given below.

– Effect of the pH

As can be seen from the figures 4 and 5, the K/S values of the cationized samples dyed with both direct and reactive dye increase as the pH of the cationization process increases. Furthermore it can be said that the effect of pH on K/S values is statistically significant ($p < 0.05$) (table 3 and 4). Improvement in the cationization degree of linen fabrics with the increase in pH of the reaction medium can be attributed to the necessity of alkaline medium for the formation of the epoxy group (figure 1) which is able to react with hydroxyl groups of fiber.

– Effect of the temperature

It is seen from the figures 4 and 5 that rise in the reaction temperature from 25°C to 75°C causes an increase in K/S value. Furthermore it can be said that the effect of reaction temperature on K/S values is statistically significant ($p < 0.05$) (table 3 and 4). Maximum K/S value of dyed samples is observed when the cationization treatment was carried out at 75°C. As previously explained by Hebeish et al., the reason of this could be associated with the positive effect of the temperature on: (a) swelling of flax fiber,

Table 3

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Concentration	2	2.9523	2.9523	1.4761	20.62	0.000
pH	2	45.8167	45.8167	22.9083	319.93	0.000
Time	2	5.9367	5.9367	2.9683	41.46	0.000
Temperature	2	18.2094	18.2094	9.1047	127.15	0.000
Error	18	1.2889	1.2889	0.0716		
Total	26	74.2038				

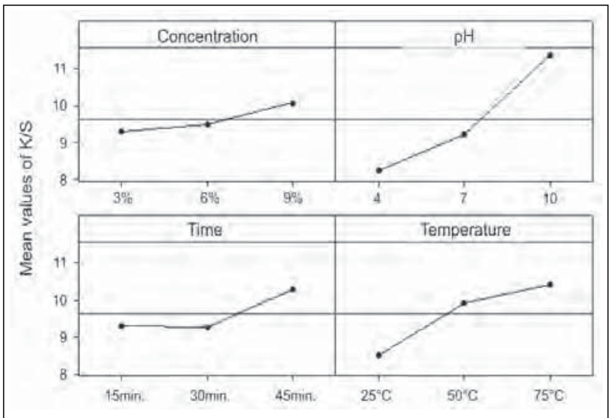

Fig. 4. Main effects plot for K/S values of linen fabrics dyed with C.I. Direct Red 80

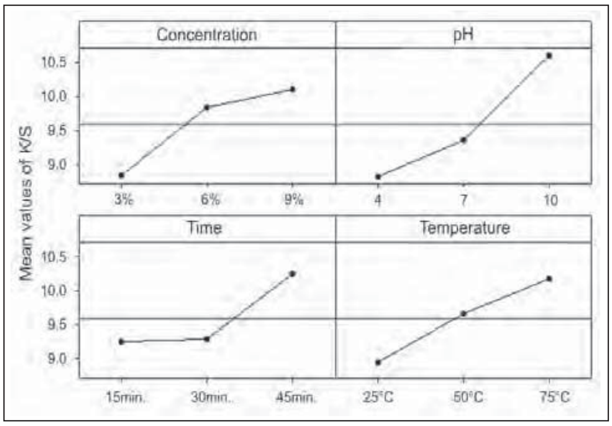

Fig. 5. Main effects plot for K/S values of linen fabrics dyed with C.I. reactive Blue 220

Table 4

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Concentration	2	8.0472	8.0472	4.0236	80.20	0.000
pH	2	15.2764	15.2764	7.6382	152.24	0.000
Time	2	5.8726	5.8726	2.9363	58.53	0.000
Temperature	2	7.0102	7.0102	3.5051	69.86	0.000
Error	18	0.9031	0.9031	0.0502		
Total	26	37.1096				

(b) diffusion of cationization agent, (c) compatibility of the reactants and (d) mobility of the cationization agent molecules and their probable collision with flax fiber macromolecules [21].

– Effect of the duration

It is seen from the figures 4 and 5 that when the reaction time is raised from 15 min. to 45 min., K/S values were increased. Furthermore it can be said that the effect of reaction time on K/S values is statistically significant ($p < 0.05$) (table 3 and 4). Maximum K/S value of dyed samples is observed when the cationization treatment was carried out for 45 minutes. As it is commonly known, for a chemical to react with a fiber there is a need of sufficient time for chemical to come in contact with fiber and to react with it. It is thought that longer time provided better opportunity for Albafix E to come in contact and react with flax fiber, and therefore, better K/S values were achieved at 45 min.

– Effect of the cationization agent concentration

It is seen from the figures 4 and 5 that rise in the cationization agent concentration from 3% to 9% increased the K/S values obtained in dyeings. Furthermore it can be said that the effect of cationization agent concentration on K/S values is statistically significant ($p < 0.05$) (table 3 and 4). As indicated before, for a chemical to react with a fiber, first it should come in contact with it. For this reason it is thought that higher cationization agent concentration increased the amount of molecules came in contact with fiber and hence higher K/S values were achieved at concentration of 9%.

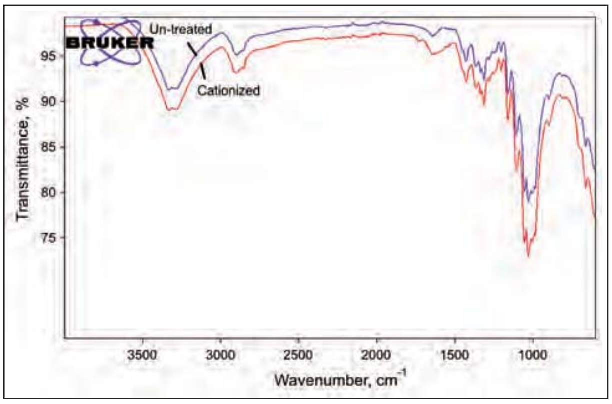

Fig. 6. FTIR spectrums of un-treated and cationized linen fabrics

Effects of cationization treatment on chemical properties of linen fabrics

Results of nitrogen content and whiteness degree analyses are listed in table 5.

Table 5

	Un-treated	Cationized
Nitrogen content (N%)	0.34	0.87
Whiteness degree (Berger)	47.60	33.39

Results of Fourier transform infrared (FTIR) and scanning electron microscopy (SEM) analyses are given in figure 6 and figure 7 respectively.

Discussions of the results are given below.

– Nitrogen content (N%)

The results given in table 5 reveal that the nitrogen content (N%) of the linen fabric increased from 0.34% to 0.87% after cationization treatment which means cationization agent is added into fiber structure. The first point that should be clarified here is that also un-treated linen fabric contains 0.34% nitrogen. Flax fibers normally contain some amount of nitrogen depending on sowing conditions, climate and maturity of plant. ***Ahmad et al.*** had given range from 0.38 to 0.91 percent for nitrogen content in flax plant [29]. On the other hand, bleaching is a necessary pretreatment step subsequent to scouring before any cellulosic material is dyed and/or finished.

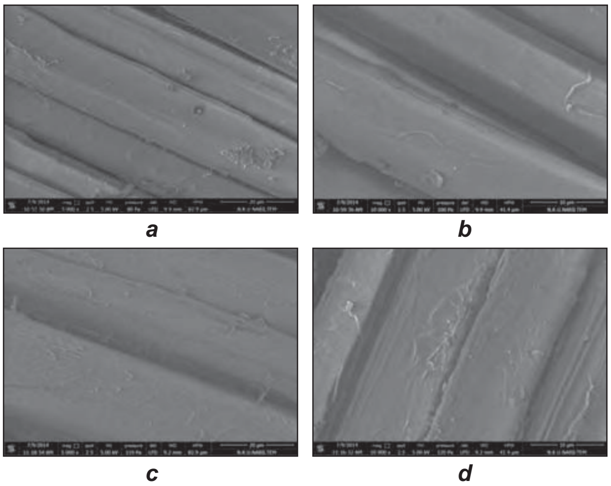

Fig. 7. SEM photographs of un-treated (*a* and *b*) and cationized (*c* and *d*) linen fabrics

During the bleaching process natural pigments and other noncellulosic matters are removed from the fibers in some extent [30]. For this reason the nitrogen content of flax fiber is normally expected to be decreased after pretreatment processes. For example; Hebeish et al. reported the nitrogen content of scoured and bleached linen fabric as 0.25% [21].

– Fourier transform infrared (FTIR) spectra

In this study, FTIR spectra were obtained for the un-treated and cationized linen fabrics as shown in figure 7. There are certain signatures that can be assigned to specific components in the fiber. The C-C ring breathing band at ~1155 cm^{-1} and the C-O-C glycosidic ether band at ~1105 cm^{-1} arise from the lignin and the polysaccharide components (that is, largely cellulose) respectively [31].

The results are very similar with the study that had been carried out on cotton fabrics with same cationization agent (Solfix E which is the former commercial name of Albafix E) by *Kamel et al.* The broad absorption band within 3332.30 and 1028.25 cm^{-1} for the un-treated linen fabric corresponds to the presence of numerous hydroxyl groups. However, the (primary-OH) band of the cationized linen became a higher intensity band within 3331.24 and 1029.14 cm^{-1} with increasing nitrogen content of the cationized fabric. These distinct high intensity bands indicate the presence of the quaternary ammonium salts. Furthermore, two splitting distinct bands can be observed in the spectrum of cationized linen fabric within 2897.84 and 2851.77 cm^{-1}, 1427.43 and 1361.97 cm^{-1}. These bands correspond to aliphatic C-H stretching, bending deformations and rocking vibrations of the methylene groups (CH_2) [32].

– Scanning electron microscopy (SEM)

In this study, SEM analyses were used to investigate the change in the surface morphology of the flax fibers after cationization treatment. Figure 7 (a) and (b) are SEM photos of the un-treated fabrics and (c) and (d) are that of the cationized ones. As it can be seen from the photos, although the surfaces of the cationized fibers are a little bit rougher compared to the un-treated samples, no significant difference exist between them. These results are compatible with observations obtained by *Wang et al.* [8]. According to these results it can be said that the physical structure of the flax fiber is almost not influenced by cationization treatment and this process can be applied to linen fabrics prior to dyeing.

– Whiteness index

Table 5 shows the change in whiteness degree of linen fabrics after cationization treatment. From table 5 it can be seen that the whiteness degree of the cationized linen fabric is lower than the un-treated one. This means yellowing occurs due to the cationization treatment. It is a well-known phenomenon that the disadvantage of cationic agents (especially the quaternary ammonium compounds) is the tendency of treated textiles to yellow. The mechanism of yellowing is thought to be associated with the quaternary ammonium groups of cationization agent. Yellowing of fabric is important from the view of dyeing, because it causes changes in nuance of dyed fabrics.

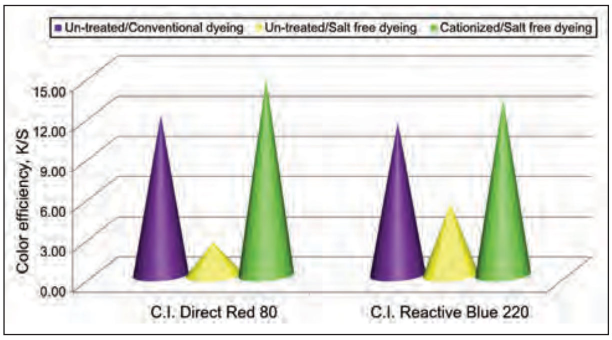

Fig. 8. Color efficiency (K/S) values of linen fabrics dyed with direct and reactive dyes

Results related to the salt free dyeability of linen fabrics

After determining the optimum conditions of cationization process, linen fabrics were treated at these conditions and then dyed with a direct and a reactive dye without salt usage. Subsequently colors of these samples were compared with conventionally dyed samples. Color efficiency values of dyed samples are given in figure 8.

As can be seen from figure 8, color efficiency values extremely decrease, if salt is not used in dyeing processes. Another striking point is that the color efficiencies were much higher in case of cationized and salt free dyed samples compared to the conventionally dyed un-treated linen fabrics. As indicated previously, when cellulosic fibers come in contact with water, they produce slightly negative charge. For this reason there is repulsion between anionic fiber and anionic dye molecules. In order to overcome this ionic repulsion, normally electrolytes are added into dye-bath. If salt is not used during dyeing, exhaustion of the dye-bath will be limited. This is why color efficiency values decrease in the absence of salt. On the other hand, when linen fabric is treated with polyaminochlorohydrin quaternary ammonium compound, it gains cationic character and hence it shows high affinity to anionic dyes. As a result, high color efficiency values could be obtained even in the absence of salt.

CIE L*a*b* values of dyed samples were also measured and results are given in table 6.

If L* values given in table 6 are examined, it can be said that L* values of cationized samples are lower than the un-treated ones. L* value is the value of lightness-darkness and the decrease of L* value shows that the color gets darker. From this point of view, the results obtained are parallel with K/S values.

When a* and b* values of un-treated and cationized linen fabrics are compared, it is understood that the difference in a* values are very small, while it is evident in case of b* values. It is seen from table 6 that

Table 6

Dye	Fabric	L*	a*	b*	C*	h
C.I. Direct Red 80	Un-treated	40,98	53,00	18,86	56,25	19,59
	Cationized	40,86	53,61	22,48	58,13	22,75
C.I. Reactive Blue 220	Un-treated	37,95	–6,05	–32,54	33,09	259,46
	Cationized	34,15	–6,69	–27,76	28,55	256,46

Table 7

Dye class	Cationization	Salt	Washing fastness						Rubbing fastness		Light fastness
			WO	PAC	PES	PA	CO	CV	Dry	Wet	
Direct	-	+	5	5	5	5	3	5	4–5	3	7
	+	-	5	5	5	5	2–3	5	3	1–2	3–4
Reactive	-	+	5	5	5	5	5	5	5	3–4	7
	+	-	5	5	5	5	5	5	3–4	2	6–7

b* values of cationized linen fabrics are higher, which means color nuances become yellowish (in other words less bluish). As it is known, the color nuance of the dyed sample is affected by the material's color prior to dyeing. The reason of change in color nuances could be understood better when whiteness degrees of un-dyed fabrics are investigated. As can be seen in table 5, whiteness degree of cationized linen fabric is lower than the un-treated one, which means its color is more yellowish. So, this is why higher b* values are obtained in case of cationized fabrics. These results reveal that in dyeing of cationized linen fabrics not only the color depth, but also the color nuance will be different from un-treated sample.

In a dyeing process another important parameter is fastness. For this reason, washing, rubbing and light fastness tests of dyed samples were carried out. Results are given in table 7.

In table 7, it is seen that washing fastness values of un-treated and cationized linen fabrics are nearly same, while rubbing and light fastness values of cationized linen fabrics are lower compared to un-treated samples. The small increase in staining on cotton in case of direct dyeing could be attributable to cationized fabric to be dyed in darker shade compared to un-treated sample.

When table 7 is investigated, it is understood that dry and wet rubbing fastness values of cationized linen fabrics are significantly lower than un-treated samples. As commonly known, cationization process increases the surface affinity of cellulose fibers to anionic dyes and this causes decrease in dye penetration. This is the consequence of reactive dye-cationic agent complex formation. Due to steric hindrance, it can block dye diffusion into the fiber and prevent access of dye molecules to functional hydroxyl groups of cotton fiber [33]. As a result, lower rubbing fastness values are obtained.

In table 7, it is seen that light fastness values of un-treated samples are fairly high. Light fastness mainly depends on a dye chromophore and dyeing depth. For this reason high light fastness values of dyed samples could be attributed to the chemical structures of dyes used in experiments. Another point that attracts attention is that the light fastness values of cationized fabrics are lower than the un-treated ones. It is a commonly known fact that one of the disadvantages of cationic products is reduced light fastness values. The decomposition of the cationic agents and the formation of free radicals and other chemicals promote the decomposition and fading of the dyes [34].

CONCLUSIONS

In this study the optimum conditions of cationization process for linen fabrics using the exhaustion method, was found to be 9% cationization agent, pH 10 and 75°C for 45 minutes. It was determined that the color efficiency was much higher in case of cationized and salt free dyed linen fabrics than the conventionally dyed samples. While the washing fastness properties were comparable, rubbing and light fastness values of cationized samples dyed without salt usage were found to be lower compared to conventionally dyed un-treated fabrics. It can be concluded that with the aid of cationization treatment prior to dyeing, salt usage could be eliminated during dyeing of linen fabrics both with direct and reactive dyes. However, the rubbing and light fastness values were moderate. This may occur depending on dye used and it should be checked before applying the cationization process. Another important point which should be taken into consideration is that the color nuances will be more yellowish in case of cationized linen fabric.

This may require adjustment of dyeing receipt in order to obtain same color nuance with that of conventionally dyed un-treated sample.

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