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Physical Modification of Lyocell® and Modal® Fabrics and its Effect on Fabric Dyeability

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THE EFFECT of some swelling agents; Viz. alkali metal hydroxides, alkaline earth metal salt and heavy metal salt, on the dyeability of lyocell and modal fabrics with reactive and direct dyes was monitored. The dyeing characteristics; namely colour strength, dyeing isotherm, diffusion coefficient, dyeing rate constant and half dyeing time of the dyed fabrics were assessed. The colour strength of the dyed samples increased in the order $ZnCl_2$ > $MgCl_2$> NaOH > KOH > untreated. The fastness properties of the dyed fabrics were investigated. X-ray diffraction patterns of both untreated as well as treated fabrics were used to assign the change in the fine structure of the swollen lyocell and modal fibres relative to their respective untreated ones. The water retention capacity of lyocell and modal fabrics was calculated to deduce the degree of crystallinty of treated as well as untreated lyocell and modal fabrics.

Keywords: Lyocell, Modal, Swelling, Dyeing, Reactive, Direct and X-ray .

Lyocell is a man-made fiber produced from wood pulp in 1987 by Courtaulds. Lyocell is completely biodegradable manufactured by an eco-friendly non-polluting process(1). Moreover, Lyocell fibres are claimed to offer environmental advantages over other regenerated fibres with regard to the recyclability of the solvent and the renewable source of cellulosic starting material(2).

Lyocell shares many properties with other cellulosic fibers such as cotton, linen, ramie and rayon. It is soft, absorbent, comfortable, very strong when wet or dry, and resistant to wrinkles; it can be machine- or hand-washed or dry-cleaned, it drapes well, and it can be dyed with many colours, as well as simulating a variety of textures like silk(3). Due to the nature of lyocell to fibrillate and take dyes poorly and unevenly, the finishing process is more complicated and takes longer than for other cellulose fabrics. Lyocell fibre has a relatively low surface energy, which makes it difficult for dyes to bind with it(4).

Modal is a man-made cellulosic fibre spun from reconstituted cellulose beech trees. It is about 50% more hygroscopic than cotton is(4).

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Although results regarding the dyeability of lyocell and modal fabrics with reactive and direct dyes have been published[5–7], a detailed study of the effect of pre-swelling in metal salts on their dyeability with reactive and direct dyes has not appeared.

Moreover it is well known that all commercial ranges of reactive dyes suffer the problem that during their exhaustive application to cellulosic fibers, the dyes undergo hydrolysis which severely reduces the efficiency of the dye-fiber reaction (fixation), resulting in wastage, and need of wash-off dyeing and major environmental problem [8].

In this investigation, an attempt has been conducted to modify the microstructure of lyocell and modal fabrics by pre-treatment with different swelling agents; namely, sodium hydroxide, potassium hydroxide, hydrated magnesium chloride and zinc chloride. Special emphasis will be devoted to the effect of these modifications on the dyeability of these fabrics with reactive and direct dyes. This would decrease the dyeing temperature and hence minimize hydrolysis of reactive dye molecules during the dyeing process.

Experimental

Material

Scoured plain weave non-fibrillating lyocell® A100 fabric and modal® fabric were kindly supplied by Lenzing AG, Austria.

Dyes

The commercial names of the used reactive dyes and their colour index (C.I.) as well as the reactive groups and manufacturers, were summarized in Table 1.

TABLE 1. Reactive and direct dyes .

Dye	C. I.	Reactive group	Manufacturer
Blue HERD	Reactive Blue 160	Bismonochloro triazine	Ria dyes & Chem. Co., India
Remazol Brilliant Yellow	Reactive Yellow 160 4GL	Vinyl sulphone	Dystar
Active Brilliant Yellow 5zkh	Reactive Yellow 1	Dichloro triazine	Shanghai Dyestuffs & Pesticides Industries, Shanghai, China
Solophonyl Red 3BL	Direct Red 80	--	Ciba Geigy

Chemicals

Sodium hydroxide, potassium hydroxide, magnesium chloride hexahydrate and zinc chloride are all of laboratory grade and used without any purification. The nonionic detergent, Hostpal CV, was purchased from I.C.I –Egypt.

Treatments

Lyocell or modal fabrics (10 g) were swollen in 250 ml of 0.1 molar aqueous solution of alkali metal hydroxides (NaOH or KOH), alkaline earth metal salt ($MgCl_2$ $6H_2O$), or transition metal salt ($ZnCl_2$), for 5 min at room temperature (ca. 30 °C).

The treated samples were passed through a padding mangle applying a pressure of 10 kg cm^{-2}, and then batched for 30 min by wrapping around a glass rod and enveloping the sample in a polyethylene sac. The samples were subsequently removed from the glass rod, rinsed with hot water for 5 min, and then rinsed with cold water for 5 min and dried at 60°C.

X-Ray diffraction pattern

The X-ray diffraction analysis was performed at room temperature for pre-swollen lyocell and modal fabrics on a Bruker D8 Avance using CUK_α as the target with secondary mono-chromator to operate at 40 KV and 40 mA. The scans were performed within the range of $4° < 2\theta < 60°$ with scanning step 0.02° in reflection geometry.

Water retention value (WRV)

Dry sample of 0.5 g of untreated as well as treated lyocell or modal fabrics were immersed in 50 ml of distilled water for 24 h. The wet samples were centrifuged at 4000 G for 10 min and the weight of the sample was recorded (W_w). The wet sample was dried at 105 ºC for 2 h and the dry weight was recorded (W_d). The water retention value (WRV) was calculated from the following equation(9):

$$WRV = \frac{W_w - W_d}{W_d}$$

Fibre diameter measurement

The lyocell and modal fabrics were pretreated with NaOH, KOH, ZnCl2, or MgCl2 $6H_2O$. The diameter of swollen fiber was measured by means of Nikon Profile Projector V-12 (Nippon Kogaku, Japan) using ASTM D276-00a (2008) test method ASTM D629 - 08 Standard Test Methods for Quantitative Analysis of Textiles.

Dyeing procedure

Dyeing with reactive dyes

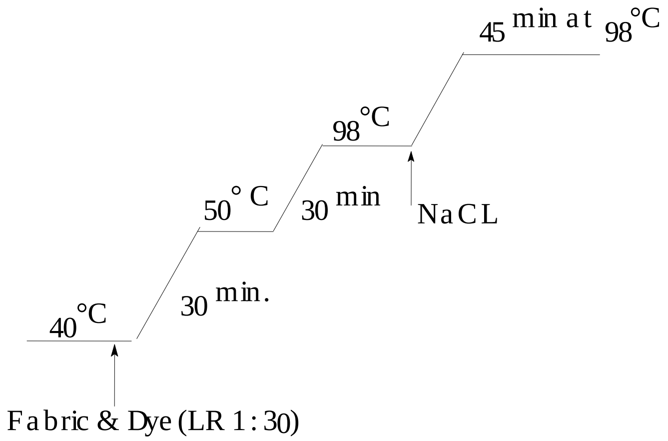
Lyocell and modal fabrics were dyed with Reactive Yellow 1, Reactive Blue 160 and Remazol Brilliant Yellow. Dyeing was carried out using 1% dye (on the weight of the fabric; owf), and liquor ratio 1:50; sodium chloride (50 g/l) was added to the dyeing bath. The temperature and pH of the dyeing bath are summarized in Table 2. Samples were introduced into the dye bath at room temperature (T_1) and pH_1. The temperature was raised gradually (2 degree/min; T_2), and the pH of the dye bath was adjusted to pH_2; the dyeing process was continued for a further 60 min. Afterwards, the dye bath temperature was reduced to 60 ºC, and then the samples were removed from the dye bath, rinsed in cold and warm water for 10 min. The dyed fabrics were rinsed with water and soaped with 5 g/l nonionic detergent, and 2 g/l sodium carbonate at 95°C for 20 min.

TABLE 2. Conditions of dyeing of lyocell and modal fabrics with reactive dyes .

Dye	T_1 (°C)	pH_1	T_2 (°C)	pH_2
Reactive Blue 160	40	4–4.5	80	8.5
Reactive Yellow 1	20	4	60	8.5
Remazol Brilliant Yellow	20	4	40	4

Dyeing with direct dye

Dyeing of lyocell and modal fabrics with the direct dye, Solophoneyl Red 3BL, was carried out by using 1% (owf) dye and liquor ratio 1:30, at pH 7-7.5. Samples were introduced into the dye bath at 40 °C and the temperature was raised gradually to 50 °C through 30 min, then to 98°C over 30 min; 15 g/l NaCl was added and the dyeing was continued at 98°C for a further 45 min, rinsed with cold water, squeezed and dried at room temperature. The samples were then soaped with non ionic detergent 3 g/l for 30 min at 60°C (see diagram below).



Time/temperature in conventional dyeing of direct dyes

Dyeing rate

Lyocell as well as modal samples were cut into pieces (approximately 1 cm^2 each) and dyed at pH 7-8 with occasional shaking. The liquor ratio was 1:30 for direct dye and 1:50 for reactive dye. Dyeing of lyocell was carried out at 60°C for direct dye and at 80°C for reactive dye, while dyeing of modal was conducted at 80°C for both classes. The liquor-to-fabric ratio was 30:1 in case of dyeing of lyocell and 1:50 in case of dyeing modal. After selected time intervals, 0.5 ml of the dye bath was pipette into test tube and diluted with distilled water to 5 ml to measure its colour absorbance at the respective λ_{max}.

Measurements

Colour strength (K/S value)

The colour strength (K/S) of the dyed fabrics was measured using Hunter lab Universal Software. Mini Scan ™ XE: RSIN using *Kubelka-Munk* equation:

$$K/S = \frac{(1 - R)}{R^2}$$

where: K, S and R are the absorption coefficient, scattering coefficient and reflectance, *respectively*.

UV/Vis absorption spectra

The UV/Vis absorption spectra in water were recorded using Shimadzu UNICAM UV 300 spectrophotometer. The quantity of dye uptake was estimated using the following equation:

$$Q = (C_0 - C_t)\, V/W$$

where Q is the quantity of dye up take (mg/g), C_o and C_t are the initial and final concentration of dye in the solution (mg/L), respectively; V is the volume of dye solution in (L) and W is the weight of the fabric (g). The concentrations of dye solution were determined after reference to the respective calibration cure of both dyes using Lambert-Beer law.

The percentage of dye exhaustion (E%) achieved for reactive dye was calculated from the following equation:

$$\%E = (A_0 - A_1)/A_0 \times 100$$

where: A_0 and A_1 are the absorbance of the dye bath before and after dyeing, respectively.

The fixation efficiency of each dyeing (%F) was calculated from the following equation:

$$\%F = (A_0 - A_1 - A^*)/A_0 \times 100$$

where A^* is the absorbance of the wash-off liquors.

From the result of the dye exhaustion and the fixation efficiency of the dye fabrics covalent bonding, the total fixation of the dye absorbed (%T) was calculated for all dyeing according to the following equation:

$$\%T = (\%F \times \%E)/100$$

Fastness testing

Fastness properties to washing[10], rubbing[11] and perspiration[12] were measured according to the standard method. Colour fastness to light was determined according to ISO test method 105-B01. The evaluation was carried out using the gray scale reference for colour change.

Results and Discussion

X-ray diffraction

X-ray diffraction patterns for the untreated and pretreated lyocell as well as modal fabric were investigated. The characteristics of two main peaks for untreated and pretreated lyocell and modal fabrics (not shown here) were clearly appeared as one intensive peak at 2θ= 22.5º and the others less intensive at 2θ=13º relative to the blank samples. The decreased intensity indicates a possible reduction in the crystallinity. Through evaluation of the area of the sharp and broad peaks, the apparent percentage of crystallinty in both treated and pretreated samples can be estimated according to the following equation: [13, 14]

$$\% C_x = \frac{IC}{Ic + Ia} \times 100$$

where $\%C_x$ is the crystallinty percentage and I_c and I_a are the intensities of x-ray diffraction pattern of crystalline and amorphous components, respectively.

TABLE 3. Effect of pre-treatment on crystallinity and d-spacing of untreated and pretreated lyocell and modal fabrics .

Treatment	Crystallinity (%)	2θ (º)	d-spacing (Aº)	Crystallinity (%)	2θ (º)	d-spacing (Aº)
	Lyocell fabric			Modal fabric		
Untreated	86.4	22.5	2.7	87.9	21	1.8
KOH	78.1	21.5	2.8	81.4	21.5	2.4
NaOH	70.4	22.5	3	77.3	22	2.5
$MgCl_2 6H_2O$	54.3	22.5	3.1	61.7	22.5	3.0
$ZnCl_2$	49.4	22.5	3	53.5	22.5	4.4

Data in Table 3 indicate that the degree of crystallinity of the pre-swollen lyocell and modal fabrics is remarkably less than those for the untreated samples. The minor change in d-spacing indicates that the alkali can permeate into the semi-crystalline and amorphous phases, leading to decrease in crystallinity and increase in water retention which leads to increase in dye exhaustion. These follow the order: $ZnCl_2$>$MgCl_2$>NaOH>KOH> untreated.

Water retention value

The water retention value (WRV) test provides an indication of fibers' ability to take up water and swell. The WRV is also highly correlated to the bonding ability of lyocell or modal fibres. The retained water is believed to be associated with submicroscopic pores within the cell wall. The WRV value equals the ratio of the water mass to the dry mass of the fibres.

Results of this investigation, summarized in Table 4, illustrate that the WRV of the treated lyocell fabrics were increased by about 2.9, 7.2, 13.0 and 14 % relative to the untreated fabrics, upon swelling the fabric with KOH, NaOH, $MgCl_2\,6H_2O$ or $ZnCl_2$, respectively. Similar results were obtained in the swollen modal fabrics. These findings rationalize the superior dyeability of the pre-swollen relative to the untreated ones.

TABLE 4. Water retention value and fibre diameter (average of 12 measurements each) of lyocell and modal fibres pretreated with different swelling agents .

Fabrics	Swelling agent	WRV (cm^3/g)	Percent increase in fibre diameter
Lyocell	Untreated	0.69	--
	Potassium hydroxide	0.71	17.72
	Sodium hydroxide	0.74	25.33
	Magnesium chloride	0.78	34.47
	Zinc chloride	0.83	48.16
Modal	Untreated	0.72	--
	Potassium hydroxide	0.75	23.8
	Sodium hydroxide	0.77	44.28
	Magnesium chloride	0.80	66.89
	Zinc chloride	0.84	68.77

Fibre diameter

Aiming to assess the degree of swelling of lyocell and modal fibres in the used swelling agents, the diameter of single fibres of the untreated as well as treated lyocell and modal was determined.

Data of Table 4 clarifies that pre-treatment of lyocell and modal fibres resulted in increase in the fibre diameter to different extent depending on the swelling agent. The percent increase in the fibre diameter, relative to the untreated one, follows the order: $KOH<NaOH<MgCl_2<ZnCl_2$. The extent of increasing the fibre diameter is higher in case of modal fibres than lyocell fibres, irrespective to the swelling agent.

Effect of swelling agents on the dyeability

The main disadvantage of lyocell fibre is its relatively low surface energy, which makes it difficult for dyes to bind to it[(4)]. Therefore, lyocell as well as modal fabrics were treated with different swelling agents, followed by dyeing with reactive and direct dyes. The effect of pre-swelling on the dyeability of lyocell and modal fabrics with reactive or direct dyes is summarized in Table 5.

TABLE 5. Effect of pre-swelling of lyocell and modal fabrics on their dyeability with reactive and direct dye (1% shade, 30 min, pH: 8.5 for Reactive Blue, Solophonyl Red (80 °C), Reactive Yellow and at pH 4 for Remazol Yellow at 40°C , 50 gm/l NaCl, 80°C, for 30 min. and L.R. 1:50)

Treatment	Colour strength (k/S)							
	Lyocell				Modal			
	Solophonyl Red	Reactive Blue	Reactive Yellow	Remazol Yellow	Solophonyl Red	Reactive Blue	Reactive Yellow	Remazol Yellow
Untreated	3.8	2.7	4.1	3.8	4.0	2.1	2.5	2.9
KOH	3.9	3.2	5.2	4.9	4.3	2.9	3.3	3.2
NaOH	3.9	3.4	5.4	5.3	4.4	3.1	4.3	3.8
$MgCl_26H_2O$	4.2	4.0	5.8	6.1	4.5	3.2	4.7	5.1
$ZnCl_2$	4.5	4.9	7.6	7.8	4.8	4.3	5.1	5.7

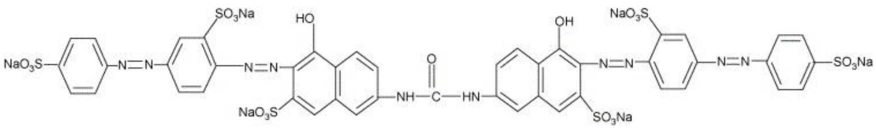
1% shade, 30 min, 40 °C, L.R. 1:50, pH 7-7.5 for Solophonyl Red, pH 4 for Remazol Yellow, pH_1 (4-4.5 for Reactive Blue, pH 4 for Reactive Yellow), pH_2: (8.5 for both Reactive Blue and Reactive Yellow).

Data of this table illustrate that pre-swelling of lyocell and modal fabrics enhances their dyeability with reactive and direct dyes to different extents depending on the substrate, dye and swelling agent. Maximum improvement in the colour strength (K/S) of the dyed fabrics was achieved in case of dyeing of lyocell fabrics, pre-swollen with zinc chloride, with Reactive Yellow 1.

Generally speaking, pre-swelling of lyocell and modal fabrics enhanced their dyeability in the order: $ZnCl_2$>$MgCl_26H_2O$>NaOH>KOH. This may be attributed to the fact that the ionic radii of the cations of alkali metals, Viz. Na^+ (102 pm) and K^+ (138 pm) are higher than those of the alkaline earth metal (Mg^{+2} 72 pm) or the transition metal (Zn^{+2} 75 pm)(15). The smaller ionic radii allow easier diffusion of the swelling agent into the fibre interior and hence, more even and effective fibre swelling. Nevertheless, the superior effect of zinc chloride in enhancing the dyeability of lyocell and modal fabrics, is due, most probably, to the ability of zinc ion, in contrary to the other used cations, to form a zinc-cellulose complex(16) which ensure durable and reproducible swelling effect.

It has been reported that swelling of lyocell and modal fabrics causes the expansion of void spaces within the semi-crystalline morphology, thus forming a water fiber two phase structure(7, 17, 18). The expansion of internal structure leads to a very high internal wetted surface area, meaning that a high proportion of the polymer hydroxyl groups become accessible to the swelling medium. The dyes are therefore transported through the void structure and can interact either physically or chemically with the available functional groups. Pre-swelling maximizes the amount of available substrate to achieve the highest uptake efficiency.

On the other hand, pre-swelling of lyocell or modal fabrics with the aforementioned reagents has limited effect on their dyeability with Solophonyl Red, presumably, due to the large molecular size of this dye (Scheme 1).



Scheme 1. Chemical structure of Solophenyl Red 3BL (C.I. Direct 80) polyazo dye .

Effect of dyeing time

The effect of the dyeing time on the K/S value of the pre-swollen dyed lyocell and modal fabrics is given in Table 6. Data of this table declared that as the dyeing time increased from 30 min up to 90 min, the K/S value of the dyed fabrics increased. The augment rate is in the order: $ZnCl_2$>$MgCl_2 6H_2O$>NaOH> KOH. It is worthy to mention that the K/S value attained a plateau after dyeing for 90 min indicating that higher dyeing time is not recommended.

Effect of dyeing temperature

The effect of dyeing temperature on the dyeability of the pre-swollen lyocell and modal fabrics with direct and reactive dye was conducted at temperature range between 40–90 ºC. Data of Table 7 clarify that the colour strength of the dyed fabrics increases as the dyeing temperature increases. Throughout the temperature range, the improvement in the dyeability of lyocell and modal fabrics with reactive and direct dyes increases in the order $ZnCl_2$>$MgCl_2$ $6H_2O$>NaOH>KOH. A plateau was attained at 60ºC in case of Reactive Yellow; at 80ºC for Reactive Blue; at 90ºC for Solophonyl Red and at 40ºC in case of Remazol Yellow dye.

Dyeing kinetics

The dyes uptake is often used to monitor changes in fiber properties brought about by variation in dyeing condition or fiber pre-treatment. Often the small variations in fibre colour are the primary indication of alteration to process variables.

Time-exhaustion-isotherm of lyocell and modal fabrics dyed with selected reactive and direct dyes are shown in Fig. 1–8. The result shows that the dye exhaustion depended on dye type, fabric, and pre-swelling treatment.

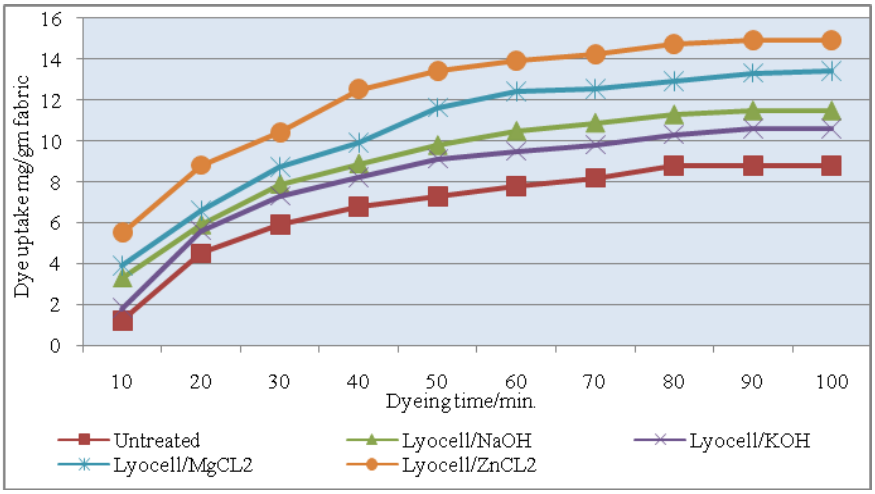


Fig. 1. Dyeing rate of lyocell dyed with Solophenyl Red 3BL. Dyeing conditions: 3% shade, L.R 1:50, 90°C at pH 7 .

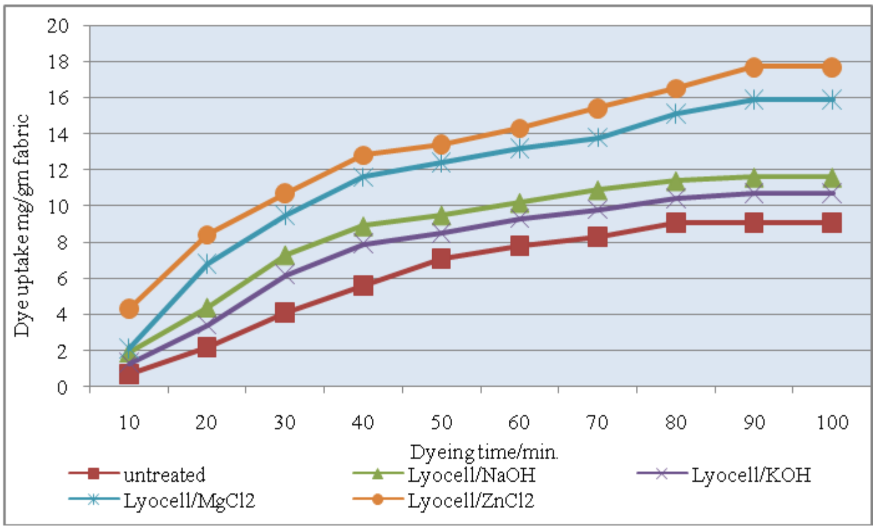


Fig. 2. Dyeing rate of lyocell fabric dyed with Remazol Red. Dyeing conditions: 3% shade, L.R 1:50, 40°C at pH_1 4 and pH_2 8.

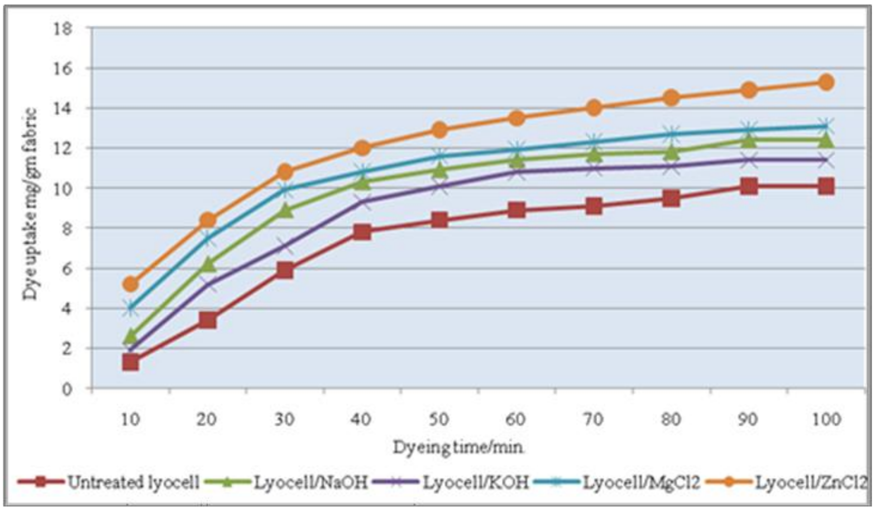


Fig. 3. Dyeing rate of lyocell fabric dyed with Reactive Yellow. Dyeing conditions: 3% shade, L.R 1:50, 60°C at pH 4 .

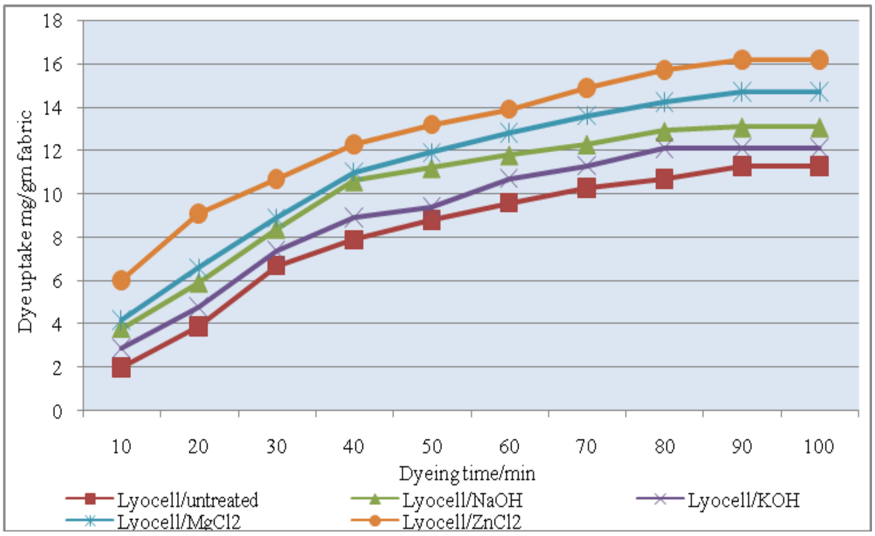


Fig. 4. Dyeing rate of lyocell fabric dyed with Reactive Blue. Dyeing conditions: 3% shade, L.R 1:50, 80°C at pH_1 4 and pH_2 8 .

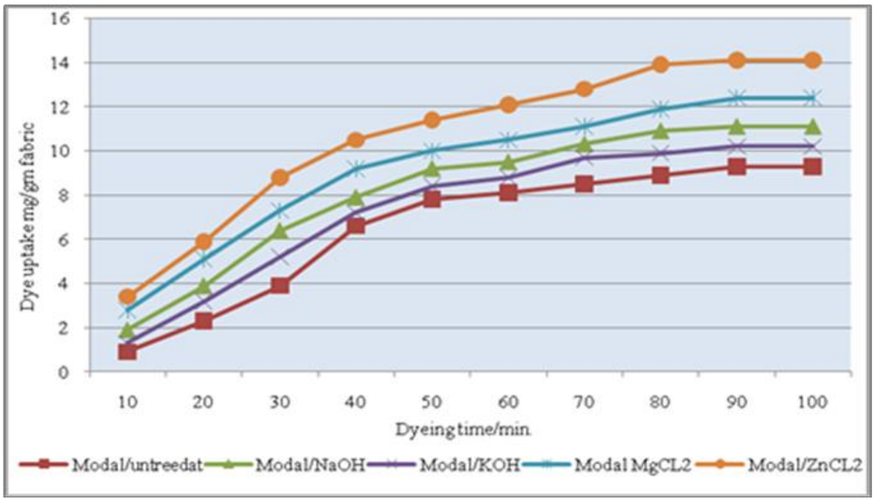


Fig. 5. Dyeing rate of modal fabric dyed with Solophenyl Red. Dyeing conditions: 3% shade, L.R 1:50, 90°C at pH 7 .

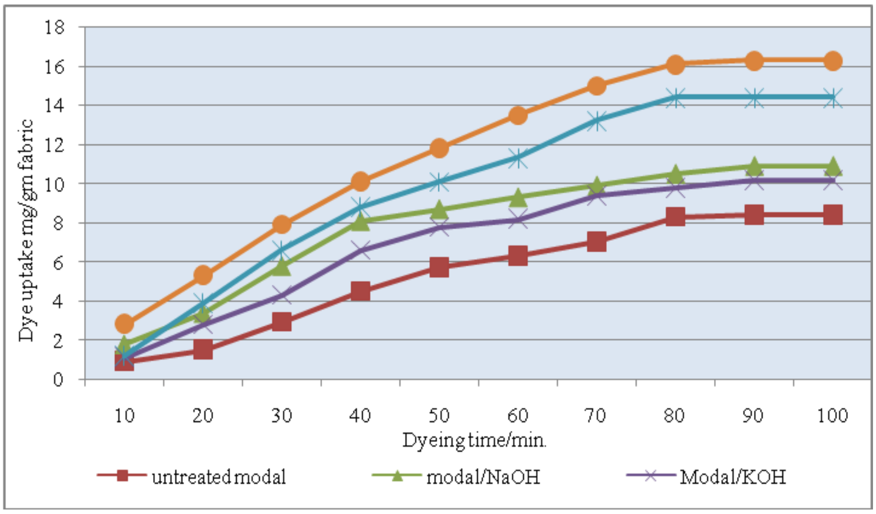


Fig. 6. Dyeing rate of modal fabric dyed with Remazol Red. Dyeing conditions: 3% shade, L.R 1:50, 40°C at pH_1 4 and pH_2 8 .

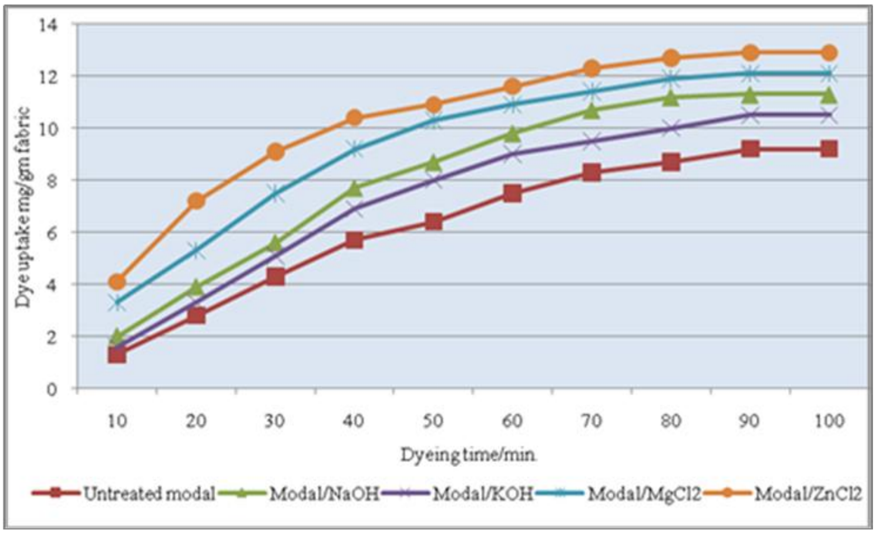


Fig. 7. Dyeing rate of modal fabric dyed with Reactive Yellow. Dyeing conditions: 3% shade, L.R 1:50, 60°C at pH 4 .

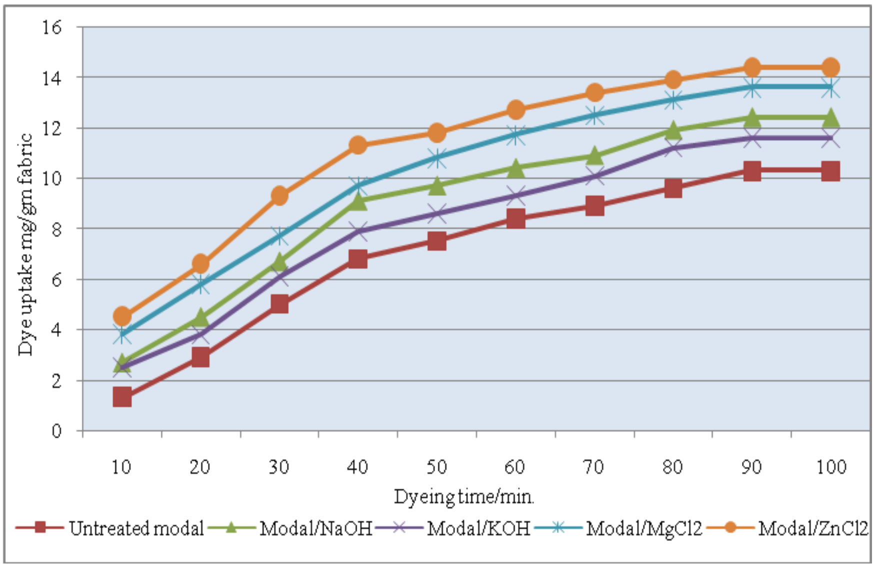


Fig. 8. Dyeing rate of modal fabric dyed with Reactive Blue. Dyeing conditions: 3% shade, L.R 1:50, 80°C at pH_1 4 and pH_2 8 .

TABLE 6. Effect of dyeing time of pre-swollen lyocell and modal fabrics on the colour intensity (K/S) in case of reactive and direct dyes .

Sample	Dyeing time/ min	K/S							
		Lyocell				Modal			
		Solophonyl Red	Reactive Blue	Reactive Yellow	Remazol Yellow	Solophonyl Red	Reactive Blue	Reactive Yellow	Remazol Yellow
Untreated	30	3.8	2.7	4.1	3.8	3,8	2.1	2.5	2.9
	60	6.6	5.7	4.6	5.2	5.1	3.9	4.2	4.8
	90	6.8	5.5	4.8	5.6	5.2	4.2	4.8	5.4
	120	6.9	5.5	5.1	5.8	5.3	4.4	4.8	5.4
KOH	30	3.7	3.2	5.2	4.9	4.3	2.9	3.3	3.2
	60	6.6	5.5	5.7	5.9	4.5	3.9	4.9	4.7
	90	7,7	6.0	5.9	6.7	5.8	4.7	5.3	5.9
	120	7.8	5.6	5.9	6.7	4.8	4.2	5.3	5.7
NaOH	30	3.8	3.4	5.4	5.3	4.4	3.1	4.3	3.8
	60	6.5	5.9	6.8	6.8	5.3	4.2	6.3	6.6
	90	7.9	6.4	7.2	7.3	5.7	5.0	6.9	7.2
	120	7.9	6.4	7.2	7.7	5.7	5.4	7.1	7.3
$MgCL_2$	30	4.3	4.0	5.8	6.1	4.5	3.2	4.7	5.1
	60	8.6	6.6	7.9	7.7	6.9	4.9	6.4	5.8
	90	8.8	6.6	7.9	8.6	7.2	5.3	6.9	6.2
	120	8.8	6.7	8.6	8.7	7.3	5.3	7.0	6.0
$ZnCL_2$	30	5.1	4..9	7.6	7.8	4.8	4.3	5.1	5.7
	60	10.9	8.8	8.9	9.9	8.9	5.4	7.5	6.6
	90	11.3	8.8	9.7	10.9	9.1	5.8	7.9	6.9
	120	11.3	8.8	9.8	10.9	9.2	6.0	7.9	7.0

1% shade, L.R. 1:50, at 80°C., pH 7-7.5 for Solophonyl Red, pH 4 for Remazol Yellow, pH_1 (4-4.5 for Reactive Blue, pH 4 for Reactive Yellow), pH_2: (8.5 for both Reactive Blue and Reactive Yellow)

The data in Fig. 1–8 can be analyzed by using the following equation:

$$A_t - A_f / A_0 - A_f = e^{-kt}$$

where A_t is the absorbance of dye bath at time t, A_0 is the initial absorbance, t is the reaction time and k is the reaction rate. Since the absorbance of solution is directly related to the concentration by Lambert-Beer law, therefore, the previous equation can be rewritten in term of dye up-take as follows:

$$Q_t - Q_f / Q_0 - Q_f = e^{-kt}$$

where Q_t is the dye uptake at time t, Q_0 is the dye uptake at zero time, and Q_f is ºthe final dye uptake, t is the dyeing time and k is the dyeing rate. Taking the logarithm of the pervious two equations would lead to the following equations and since Q, is known as Q_t - Q_f.

$$Ln\left|Q_t - Q_f\right| = Ln\left|Q_o - Q_f\right| - kt$$

A plot of $ln\ Q_t - Q_f$ vs time is expected to be linear with a slope of k. The linear of the last equation holds indeed to both fabric and the value of dyeing rate constant were obtained, as listed in Tables 7 and 8.

TABLE 7. Effect of dyeing temperature on colour strength of pre-swollen lyocell and modal fibres when dyed with reactive and direct dyes .

Temp.(°C)	Sample	K/S							
		Lyocell				Modal			
		Solophonyl Red	Reactive Blue	Reactive Yellow	Remazol Yellow	Solophonyl Red	Reactive Blue	Reactive Yellow	Remazol Yellow
40	untreated	0.9	1.0	1.1	6.6	0.8	0.6	1.2	6.4
	KOH	1.0	1.0	3.8	7.7	1.2	0.7	2.1	7.0
	NaOH	1.1	1.0	4.5	8.3	1.6	0.8	2.4	7.8
	$MgCl_2$	2.8	1.2	4.6	8.8	2.1	1.0	3.5	7.9
	Zn Cl_2	4.7	2.4	4.9	11.0	2.7	1.4	4.4	8.0
60	untreated	3.4	2.2	6.8	6.3	1.6	1.3	5.8	6.0
	KOH	4.5	3.4	5,9	7.4	3.5	2.2	5.8	5.6
	NaOH	4.9	4.0	7.7	7.7	4.1	2.5	6.9	7.3
	Mg Cl_2	9.1	4.3	8.4	8.7	4.6	3.0	6.9	6.3
	Zn Cl_2	11.4	5.6	9.8	10.5	6.0	3.7	7.9	6.6
80	untreated	6.8	5.5	4.8	5.6	5.2	4.2	4.8	5.4
	KOH	7.7	6.0	5.9	6.7	5.8	4.7	5.3	5.9
	NaOH	8.0	6.4	7.2	7.3	5.7	5.0	6.9	7.2
	Mg Cl_2	8.8	6.6	7.9	8.6	7.2	5.3	6.9	6.2
	Zn Cl_2	11.3	8.8	9.6	10.9	9.1	5.8	7.9	6.9
90	untreated	7.4	2.2	1.3	1.0	5.7	3.0	2.0	0.8
	KOH	6.1	3.1	2.6	1.0	5.6	2.7	1.9	2.1
	NaOH	8.0	4.4	3.3	2.6	6.8	3.5	2.8	2.2
	Mg Cl_2	9.1	4.4	3.8	3.2	8.7	4.3	3.5	2.0
	Zn Cl_2	11.2	5.1	3.8	3.5	10.2	4.7	3.8	2.1

1% shade, 90 min., L.R. 1:50, pH 7-7.5 for Solophonyl Red, pH 4 for Remazol Yellow, pH_1 (4-4.5 for Reactive Blue, pH 4 for Reactive Yellow), pH_2: (8.5 for both Reactive Blue and Reactive Yellow).

The time of half dyeing ($t_{1/2}$) which is the time required for the fabric to take up half of the amount of dye taken at equilibrium, is estimated from each isotherm directly (Fig. 1–8) and/or from the following equation:

$$t_{1/2} = ln\,2/k$$

TABLE 8. Dyeing rate constant K, half dyeing time ($t_{1/2}$), standard affinity -Δμ and amount of final dye uptake by lyocell and modal fabric using Solophonyl Red and Reactive Blue .

Fabric	Solophonyl Red				Reactive Blue			
	K (min^{-1})	-Δμ (KJ/mol)	$t_{1/2}$ (min)	Q_f (mg/g)	K (min^{-1})	-Δμ (KJ/mol)	$t_{1/2}$ (min)	Q_f (mg/g)
Lyocell								
Untreated	2.882	-23.209	3.7	9.5	2.888	-19.631	3.6	10.1
KOH	2.812	.-20.0156	3.6	10.2	2.851	-17.074	3.5	10.7
NaOH	2.854	-15.200	3.4	11.5	2.812	-13.354	3.4	11.6
$MgCl_26H_2O$	2.705	-6.462	3.0	13.4	2.532	3.478	2.4	15.9
$ZnCl_2$	2.696	-5.244	3.0	13.7	2.409	10.535	1.9	17.7
Modal								
Untreated	2.959	-24.144	3.9	9.3	2.914	-22.711	3.8	9.4
KOH	2.889	-20.465	3.7	10.1	2.876	-2.702	3.6	10.2
NaOH	2.835	-16.060	3.5	11.1	2.846	-16.237	3.5	10.9
$MgCl_26H_2O$	2.766	-10.568	3.2	12.4	2.639	-2.317	2.8	14.4
$ZnCl_2$	2.665	-3.626	2.9	14.1	2.510	5.030	2.3	16.3

TABLE 9. Dyeing rate constant K, half dyeing time ($t_{1/2}$), standard affinity -Δμ and amount of final dye uptake by lyocell and modal fabric using Reactive Yellow and Remazol Brilliant Yellow.

Fabric	Reactive Yellow				Remazol Brilliant Yellow			
	K (min^{-1})	-Δμ (KJ/mol)	$t_{1/2}$ (min)	Q_f (mg/g)	K (min^{-1})	-Δμ (KJ/mol)	$t_{1/2}$ (min)	Q_f (mg/g)
Lyocell								
Untreated	2.809	-12.598	3.4	11.6	2.771	-10.051	3.3	12.1
KOH	2.808	-11.451	3.4	11.9	2.785	-9.342	3.3	12.3
NaOH	2.774	-9.563	3.3	12.4	2.731	-5.843	3.1	13.3
$MgCl_26H_2O$	2.731	-6.955	3.1	13.1	2.628	-1.027	2.7	14.7
$ZnCl_2$	2.585	-1.092	2.6	15.3	2.525	-4.115	2.3	16.2
Modal								
Untreated	2.879	-18.112	3.6	10.2	2.825	-12.928	3.5	11.3
KOH	2.864	-15.317	3.6	10.9	2.804	-11.841	3.4	11.6
NaOH	2.827	-13.755	3.5	11.3	2.762	-8.988	3.2	12.4
$MgCl_26H_2O$	2.788	-10.693	3.3	12.1	2.696	-4.805	3.1	13.6
$ZnCl_2$	2.736	-7.696	3.1	12.9	2.646	-2.0544	2.8	14.4

The values of half dyeing ($t_{1/2}$) are given in Tables 8 and 9. The rate constant of dyeing lyocell and modal fabrics using selected dyes increased apparently upon pre-swelling compared to the untreated one. Moreover, the values of ($t_{1/2}$) of dyeing in case of the pre-swollen fabrics are significantly smaller than those of untreated one. Again, this may be attributed to swelling action of the used reagent which increases the size of the crystalline domains that make up the fibrillar texture, leading to void a corresponding expansion of interfibrillar void spaces. This would be expected to raise water retention value [19]. It is worth mentioning that the findings of this investigation are in harmony with the results of X-ray diffraction patterns of the dyed lyocell and modal fabrics.

Standard affinity

Standard affinity is the difference between the chemical potential of the dye in standard state on the fiber and the corresponding chemical potential in its standard tendency to move from the solution to the fiber when it is in its standard state in each phase. The standard affinity can be calculated using the following equation.

$$-\Delta\mu = RT\ln\frac{[c]_f}{[c]_s}$$

where R is the gas constant, T is the absolute temperature, $[C]_f$, and $[C]_s$ is dye concentrations in the fibre and the dye bath, respectively. From data of Tables 10 and 11, it is clear that the standard affinity of the pre-swollen lyocell and modal fabrics is higher than that in case of untreated. The chemical basis of the interaction is not fully understood, but is likely to involve Van-der-Waals attractions between fabric hydroxyl groups and dye aromatic π-system. In addition, it is possible that the hydroxyl groups disrupt the water hydration layer around the dye reducing its solubility and bringing it closer to the fabric surface [20].

Exhaustion, total fixation efficiency and dye fixation of dye absorbed for lyocell and modal fabric dyed with direct and reactive dye are shown in Tables 11 - 14. From the results we noticed that the total fixation percent of direct dye is less than the reactive dye this may be attributed to the reaction of dyes with lyocell and modal fabric.

TABLE 10. Exhaustion percentage (%E), total fixation efficiency (%T) and the fixation (%F) of dye absorbed for lyocell and modal fabric dyed with Reactive Blue .

Fabric	%E	%T	%F	%E	%T	%F
	Lyocell fabric			**Modal fabric**		
Untreated	34	27	79.4	31	20.6	66.5
KOH	60.0	48.6	81.0	57.3	44.1	77.0
NaOH	63.0	52.3	83.0	60.2	47.5	78.9
$MgCl_2 6H_2O$	71.6	63.3	88.4	69.3	55.7	80.3
$ZnCl_2$	87.7	78.7	89.7	72.6	60.6	83.5

TABLE 11. Exhaustion percent (%E), total fixation efficiency (%T) and the fixation (%F) of dye absorbed for lyocell and modal fabrics dyed with Reactive Yellow.

Fabric	%E	%T	%F	%E	%T	%F
	Lyocell fabric			Modal fabric		
Untreated	34.2	26.1	76.3	31.3	22.5	65.6
KOH	63.1	51.5	81.6	58.0	45.7	78.8
NaOH	64.4	53.6	83.2	61.0	49.1	80.5
$MgCl_2 6H_2O$	72.3	64.4	89.1	70.1	59.5	84.9
$ZnCl_2$	82.6	75.6	91.5	73.4	62.5	85.2

TABLE 12. Exhaustion percentage (%E), total fixation efficiency (%T) and the fixation (%F) of dye absorbed for lyocell and modal fabric dyed with Remazol Brilliant Yellow.

Fabric	%E	%T	%F	%E	%T	%F
	Lyocell fabric			**Modal fabric**		
Untreated	35.6	27.3	67.7	32.4	22.8	70.4
KOH	64.0	52.5	82.0	58.6	46.5	79.4
NaOH	65.3	55.1	84.4	61.4	49.7	81.0
$MgCl_2 6H_2O$	73.4	65.8	89.6	70.7	60.1	85.0
$ZnCl_2$	82.7	76.4	92.3	74.1	63.5	85.7

TABLE 13. Exhaustion percent (%E), total fixation efficiency (%T) and fixation (%F) of dye absorbed for lyocell and modal fabrics dyed with Solophonyl Red.

Fabric	%E	%T	%F	%E	%T	%F
	Lyocell fabric			**Modal fabric**		
Untreated	30.7	20.5	67.2	31	19.6	63.2
KOH	38.3	27.3	71.3	37	25.1	67.9
NaOH	36.0	28.3	78.6	33.7	26.0	77.2
$MgCl_2 6H_2O$	44.7	37.7	84.3	41.3	33.8	81.8
$ZnCl_2$	49.7	44.3	89.2	47	40.4	86.0

Fastness properties

It is clear from the data listed in Tables 14 and 15 that the fastness properties depend on the fabric type and dyes used. The rubbing, washing and perspiration fastness ranged from good to excellent in case of using preswelling fabric, while the ranges were from poor to good in case of using untreated one. All the dyed fabrics have excellent fastness to light.

TABLE 14. Fastness properties of dyed modal fabric: Solophonyl Red: pH 7, 90°C Reactive Blue pH 8, 80°C, Reactive Yellow pH 8, 60°C, and Remazol Yellow pH 4, 40°C. (3% shade, L.R 1:50, 50 gm/l NaCl 1.5 h)

Dyes	Treatment	Washing fastness				Rubbing Fastness		Perspiration fastness				Light fastness
		60°c		80°c		Dry	Wet	Alkaline		Acidic		
		Alt	St	Alt	St			Alt.	St	Alt	St	
Slphonyl Red	Untreated	3	2-3	2-3	3	3	3	2-3	3	3	2	5
	KOH	3-4	3	3	3	3-4	3-4	2-3	3	3	2-3	5
	NaOH	3-4	3	3	3	4	4	3	3	2-3	2-3	5-6
	$MgCl_26H_2O$	4	4	4	4	4	4	3	3	3	3	5-6
	Zn Cl_2	4	4	4	4	4	4	3	3	3	3	6
Reactive Blue	Untreated	2-3	2-3	2-3	2-3	3	3	2-3	2-3	2-3	2-3	4-5
	KOH	3	3	3	3	3	3	2-3	2-3	3	3	5
	NaOH	3-4	3-4	3	3	3	3	3-4	3-4	3	3	5-6
	$MgCl_26H_2O$	4	4	3-4	3-4	4	4	3-4	3-4	3	3	5-6
	$ZnCl_2$	4	4	4	4	4	4	3-4	3-4	3-4	3-4	6
Reactive Yellow	Untreated	2-3	2-3	3	3	2-3	2-3	2	2	2-3	2-3	5-6
	KOH	3	3	3	3	2-3	3	3	3	3	3	6
	NaOH	3-4	3-4	3-4	3-4	4	3-4	4	4	3-4	3-4	6
	$MgCl_26H_2O$	4	4	4	4	4	4	4	4	4	4	6-7
	$ZnCl_2$	4	4	4	4	4	4	4	4	4	4	6-7
Remazol Yellow	Untreated	3	3	3	3	3	3	2-3	2-3	2	2	5-6
	KOH	4	4	3-4	3-4	3-4	3-4	3-4	3-4	3	3	6
	NaOH	4	4	4	4	3-4	3	3	3	3	3	5-6
	$MgCl_26H_2O$	4	4	4	4	4	4	3-4	3-4	4	4	6-7
	$ZnCl_2$	4	4	4	4	4-5	4-5	4	4	4	4	6-7

TABLE 15. Fastness properties for lyocell fabric (for Direct (pH=7, 90°C), Reactive Blue pH 8, 80°C), Reactive Yellow (pH 8, 60°C), Remazol Yellow (pH 4, 40°C), 3% shade, L.R 1:50, 50g/l NaCl, 1.5 h .

Dyes	Treatment	Washing fastness				Rubbing Fastness		Perspiration fastness				Light fastness
		60°c		80°c		Dry	Wet	Alkaline		Acidic		
		Alt	St	Alt	St			Alt.	St	Alt	St	
Slphonyl Red	Untreated	2-3	2-3	2	2	3	3	3	3	3	3	5-6
	KOH	3	3	3	3	3	3	2-3	2-3	2-3	3	6
	NaOH	3-4	3-4	3	3	4	4	3-4	3-4	4	4	6
	$MgCl_2$	4	4	4	4	4	4	3-4	3-4	4	4	6-7
	$ZnCl_2$	4-5	4-5	4	4	4-5	4	4	4	4	4	6-7
Reactive Blue	Untreated	3	3	3	3	3	2-3	2-3	2-3	2-3	2-3	5
	KOH	3	3	3-4	3-4	3	3	3	3	3	3	5
	NaOH	3	4	4	4	3-4	3-4	3-4	3-4	3	3	5-6
	$MgCl_2$	4	4	3-4	3-4	4	4	3-4	3-4	3-4	3-4	5-6
	$ZnCl_2$	4	4	4	4	4-5	4-5	4	4	4-5	4-5	6
Reactive Yellow	Untreated	3	3	3	3	2-3	2-3	3	3	3	3	5-6
	KOH	3	3	3	3	3	3	3-4	3-4	3-4	3	5-6
	NaOH	3-4	3-4	3-4	3-4	3-4	4	3	3	3	3	5-6
	$MgCl_2$	4	4	4	4	4	4	3-4	3-4	4	4	6
	$ZnCl_2$	4	4	4	4	4	4	4	4	4	4	6
Remazol Yellow	Untreated	3	3-4	3-4	3	3	3	3	3	3	3	5-6
	KOH	4	4	4	3-4	3-4	4	4	4	4	4	6
	NaOH	3-4	3-4	3-4	4	4	4	3-4	3-4	4	4	6-7
	$MgCl_2$	4-5	4-5	4-5	4	4	4	4	4	4	4	6-7
	$ZnCl_2$	4	4	4	4	4	4	4-5	4-5	4-5	4-5	6-7

Conclusion

The dyeability of both lyocell and modal fabrics with reactive and direct dyes can be enhanced by pre-swelling in dilute aqueous solutions of caustic soda, caustic potash, hydrated magnesium chloride or zinc chloride. Using equi-molar amounts of the swelling agents, the extent of improvement in dyeability of lyocell and modal fabrics was in the order: $ZnCl_2$>$MgCl_2 6H_2O$>NaOH<KOH, irrespective to the substrate. The dyeing time and temperature of lyocell and modal fabrics can be lowered significantly upon swelling of the said fabrics with either magnesium chloride or zinc chloride. This would make these reagents of considerable economic importance to the dyers of both lyocell and modal fabrics.

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تحويرات فيزيقية على أقمشة الليوسِل والمودال وتأثيرها على قابليتها للصباغة

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تم دراسة تأثير معالجة أقمشة الليوسل (Lyocell) والموادال (Modal) ببعض المواد المسببة لإنتقاخ الألياف مثل هيدروكسيد عناصر الأقلاء (Alkali metal hydroxides)، هيدروكسيد عناصر الأقلاء الأرضية (Alkaline earth metal hydroxide)، ملح معدن ثقيل (Heavy metal salt) على قابليتها للصباغة بالصبغات النشطة والمباشرة. لذا فقد تم تعيين شدة اللون، منحنى الصباغة الحراري (dyeing isotherm)، معامل الإنتشار، ثابت معدل الصباغة، فترة عمر النصف للأقمشة المصبوغة المعالجة وغير المعالجة. وقد لُوحِظ زيادة شدة اللون للأقمشة المصبوغة حسب الترتيب التالي:
$ZnCl_2$>$MgCl_2$>NaOH>KOH>untreated مع تحسن ملحوظ في درجة ثبات الأقمشة المعالجة المصبوغة بالمقارنة لتلك غير المعالجة. كما تم دراسة التغيير الحادث في التركيب البللوري الدقيق لألياف الليوسل والمودال المعالجة باستخدام الأشعة السينية (X-Ray diffraction pattern). كما تم تعيين درجة التبلر في الأقمشة المعالجة وفير المعالجة من خلال قياس سِعة الإحتفاظ بالماء (Water retention capacity) للعينات المذكورة.

وبصغة عامة، يمكن القول بأن معالجة أقمشة الليوسل والمودال بالمواد المسببة للإنتفاخ قد أدت إلى إنخفاض ملحوظ في درجة حرارة وزمن عملية الصباغة بصبغات نشطة ومباشرة مما أدى إلى وفر في تكلفة المنتج النهائي، تقليل الصبغات المنصرفة في المجاري المائية، الحد من التحلل المائي الحادث لبعض الصبغات النشطة عند إجراء عملية الصباغة عند درجات حرارة أعلى.