

Part A: English Edition

Journal of Textiles and Polymers



Vol. 10, No. 3, 3-12, July 2022

ORIGINAL PAPER

Innovative Method for Demineralization of Cellulosic Substrates via Morpholinium Hydrogen Sulfate

Jalal Rahmatinejad, Akbar Khoddami*, Amir Abdolmaleki, and Hossein Izadan

Received: 26 November 2021, Accepted: 12 March 2022

Abstract- Currently, replacement of hazardous chemical treatments with environmentally-friendly alternatives coupled with assimilation of different processes in one step in order to save water and energy and prevent the production of waste is one of the priorities of industries that seek sustainable development and cleaner production. Conventional demineralization of cotton fabric is mostly carried out using mineral acids which are corrosive, toxic, and above all, could cause fabric damage. In addition, demineralization as a separate step requires a high rate of water and energy consumption. This study examines the possibility of simultaneous desizing and demineralization using an acidic and nonvolatile ionic liquid. Evaluation of different experimental conditions revealed that under proper condition via morpholinium hydrogen sulfate, simultaneous demineralization and starch desizing of the cellulosic substrate could be carried out with a significant decrease in the concentration of cationic metal ions like Fe²⁺, Cu²⁺, Mg²⁺, Ca^{2+} , and Zn^{2+} while the quality of desizing is at the same range as conventional enzymatic hydrolysis (Tegewa: 8-9). This new method did not show any negative effects on the substrate tensile properties.

Keywords: demineralization, desizing, cotton fabric, starch, cationic metal ions

I. INTRODUCTION

Constituents such as amino acids, proteins, wax, pectic

J. Rahmatinejad, A. Khoddami, and H. Izadan

Department of Textile Engineering, Isfahan University of Technology, P.O. Box 84156-83111, Isfahan, Iran.

A. Abdolmaleki

Department of Chemistry, Isfahan University of Technology, P.O. Box 84156-83111, Isfahan, Iran.

Correspondence should be addresses to A. Khoddami e-mail: khoddami@cc.iut.ac.ir

substances, organic acids, sugars, and pigments [1,2]. Besides, in sizing as a crucial step for weaving, starch and lubricants are necessary to be applied on the warp yarn before weaving [3,4]. Sizing materials and non-cellulosic impurities have adverse effects on some properties of cotton like wettability. Subsequently, these problems necessitate appropriate pretreatment processes, including desizing, scouring, and bleaching to efficiently eliminate harmful materials. Otherwise, dyeing and further finishing procedures of the product would be negatively affected [3,5].

Inorganic cations as the salts of organic acids or inorganic anions are other non-cellulosic impurities in the structure of cotton. During the growth of cotton, the plant absorbs metals like potassium from soil as nutrients. Furthermore, soil (including potassium, calcium, copper, selenium, chromium, mercury, and nickel) and plant parts (including calcium, phosphorus, sulfur, potassium, and iron) may be incorporated into lint, particularly in agricultural processes like harvesting [2]. Some of the earth alkalis can result in problems in the peroxide bleaching step by catalyzing the decomposition of perhydroxyl anions and making it ineffective. Also, severe decomposition of the peroxide can cause catalytic damage to the product [6,7]. In addition, this kind of impurities can interfere with dyeing and may cause yellowness and create other undesirable colors on the fabric [2]. Demineralization is a substantial process that can lead to better evenness and more brilliant dyeing, decrease waste of peroxide and ash content and increase the whiteness of final textile. Moreover, demineralization prevents the catalytic damage of fibers. Elimination of metals from the structure of textiles can be done by converting them to the corresponding water-soluble salts using inorganic acids. Also, utilization sequestering agents can be effective for this purpose [8,9].

In acid steeping desizing method, there is the possibility of chain session and severe damage of the glucosidic polyacetal, structure of the cellulose. Also, not being environmentally friendly made this method less common than it used to be [10,11]. Enzymatic desizing is the most common cotton desizing method owing to the fact that it has a specified reaction on starch without any destructive effect on the cellulosic structure of cotton. Nevertheless, in addition to the limited shelf life of enzymes, this method has some other disadvantages, such as downstream processing problems and sensitivity of enzymes to operational conditions like temperature, pH, and presence of metal ions [12,13]. Besides, demineralization, despite its advantages, is not considered as a main step of cotton preparation and is mostly avoided since it requires an additional processing step and increases the total cost of production. Moreover, using mineral acids in demineralization bath as the most common method could extremely reduce the substrate tensile properties. Accordingly, an inexpensive alternative combined desizing and demineralization method without limitations of the conventional desizing process, which provides high efficiency of both procedures, would be very reasonable. Dehabadi et al. have introduced a combination of acid demineralization and enzymatic desizing using citric acid and acid-tolerant enzymes [6].

Ionic liquids (ILs) are defined as liquids that are solely composed of anion and cations and their melting point is below 100 °C [14]. Nowadays, these liquids, because of being safe and environmentally-friendly solvents are considered as a potential alternative for conventional volatile organic solvents. ILs have the ability to dissolve a variety of organic and inorganic compounds and have favorable properties like negligible vapor pressure, wide liquid range, chemical and thermal stability, tunability for specific tasks, low flammability, high ionic, and thermal conductivity [14-16]. Recently, Brønsted acidic ionic liquids are increasingly considered an alternative for conventional mineral acids in chemical processes. Separation and recovery of conventional mineral acids, such as sulfuric acid and hydrochloric acid from the product are difficult. Also, these acids are toxic and corrosive and can damage the body of the apparatus and products. But, Brønsted acidic ionic liquids are very selective in reactions and highly recoverable [17,18]. Morpholinium hydrogen sulfate ([Mor-H]HSO₄) is an inexpensive, highly stable, and recoverable Brønsted acidic ionic liquid that has a mild acidic characteristic [19-21]. Above all, in our recent article, the merit of this ionic liquid as a novel desizing agent has been demonstrated [22]. In this research, the possibility of demineralization of cotton fabric during starch desizing via

[Mor-H]HSO₄ as a new, reasonably priced and efficient method is investigated and compared with conventional methods. Under such conditions, a new treatment method is introduced, that combines two processes to save water, time, and energy and decreases the related wastewater.

II. EXPERIMENTAL

A. Materials

The fabric (100% cotton, 170 g/m²) was supplied by Hejab textile Co., Iran. The warp yarns of this fabric were covered via corn starch as sizing material. Morpholine, sulfuric acid, sodium silicate, hydrogen peroxide, sodium carbonate, acetic acid, and sodium hydroxide were of analytical grade from Merck, Germany. Sera wet CN-R non-ionic detergent was obtained from DyStar and α -amylase enzyme was manufactured from Gk Biochemical Corporation, India. Direct Red 12B (C.I. Direct Red 31) was provided by Youhao, China. The [Mor-H]HSO₄ was synthesized using morpholine and sulfuric acid in accordance with the method that has been described in our previous articles [22-24].

B. Preparation of Samples

Desizing of the cotton fabric samples was carried out using the synthesized ionic liquid as a novel desizing agent and conventional α -amylase enzyme. In desizing via [Mor-H]HSO₄, samples were treated in a bath with a liquor to good ratio of 40:1 with different concentrations of [Mor-H]HSO₄ (0.25 and 0.5 w/v%), under various conditions including two levels of temperatures (70 and 95 °C) and treatment times (20 and 80 min). Treatment conditions and the identification code of each sample are shown in Table I. After desizing, warm washing and cold rinsing for 10 min were carried out to remove the remnants of the sizing materials.

Simultaneous scouring and bleaching of desized samples were carried out under the following conditions: 5 g/L hydrogen peroxide (35%), 0.4 g/L sodium carbonate, 0.4 g/L sodium hydroxide, 1.4 g/L sodium silicate, with a liquor to good ratio of 40:1, at boiling temperature for 2 h. After scouring and bleaching, the samples were washed (hot, warm, and finally cold washing) and neutralized by a solution of 0.1% acetic acid. After the combined scouring and bleaching step, dyeing of the pretreated samples was carried out. The dyeing equipment was a Polymat dyeing machine (Ahiba 1000, Datacolor, Switzerland). Dyeing bath included: 1% dye, 20% sodium chloride; with a liquor to good ratio of 40:1. Similar to the normal dyeing process, the dyeing of the samples was started at 40 °C, then the temperature was increased to 60 °C with a rate of 1 °C/min and the dyeing was continued for 40 min at 60 °C. Finally, the dyeing was completed by rinsing with cold water and drying at ambient temperature.

C. Evaluation of Desizing Quality

Before each test, the samples' conditioning process was carried out for 24 h under standard atmosphere (20 °C, 65% relative humidity). The quality of the starch removal process was investigated by iodine test, weight loss and scanning electron microscopy (SEM).

C.1. Iodine Test

The quality of starch desizing was evaluated by TEGEWA scale method. In this pictorial test, the amount of starch on the fabric surface is determined by the appeared color after adding iodine droplets. A rating between 1 and 9 is awarded by identifying which one of the nine pictures on the TEGWA scale has the same color as the sample under test after impregnation with iodine solution. TEGEWA 1 denotes extremely poor starch desizing whilst a rating of 9 is deemed not to have any residue of the starch. TEGEWA 6 or higher indicates the acceptable quality of the desizing process [5,25].

C.2. Weight Loss

The gravimetric evaluation of the amount of removed size was carried out by measuring the weight of the samples (with precision of 0.0001 g) before and after desizing using Eq. (1). Before weighing, the samples were completely dried by a laboratory oven:

$$W.L\% = ((w_1 - w_2) / w_1) \times 100$$
(1)

where W.L is the weight loss, and w_1 and w_2 refer to the weight of the sample before and after the desizing step, respectively.

C.3. Scanning Electron Microscopy (SEM)

SEM micrographs were taken by a Philips scanning electron microscope (XL 30 Japan) in order to investigate the morphology of the fibers and starch remnants on their surface. Before imaging, the samples were coated with a layer of gold using a sputter coating machine (SCD 005, Bal-tec, Switzerland).

D. Concentration of Cationic Metals

The concentration of cationic metals including iron, copper, magnesium, calcium, zinc, sodium, potassium, and manganese was measured using an inductively coupled plasma optical emission spectrometer (Optima 7300 DV, Perkin Elmer, USA). For this purpose, 1 g of the sample was digested in 20 mL of nitric acid (65%); then, the solutions were diluted by deionized water.

E. Strength of Samples

Tensile strength of fabrics was determined using the constant rate of extension (CRE) of a tensile testing machine (Zwick Universal Testing Machine 144660, Germany) according to the ASTM D 5035 breaking strength and elongation of textile fabrics-strip method, with 150 mm gauge length and 100 mm/min crosshead speed. The average values with 95% confidence intervals and one-way ANOVA are reported.

F. Water Absorbency

F.1. Wetting Time

The wetting time of samples was performed in accordance with AATCC 79-2010. According to this method, a distilled water droplet was allowed to fall from a fixed height on the sample surface. The time required for absorbing the drop (losing light reflection characteristic of the drop) was recorded as wetting time. The test was repeated in 10 different points of each sample and the average was reported. The number 0 refers to extremely fast absorption (less than one second) and in cases where wetting time exceeds 1 min, the result is recorded as "60+".

F.2. Vertical Wicking

AATCC 197-2012 was used for measuring vertical wicking properties of the samples (the ability of the samples to transport liquid in a vertical position). The results of this test are recorded as an average wicking distance of 3 runs for each sample in 5 min.

G. Whiteness Index

CIE 1982 formula under D65 standard illuminant with CIE 1964 (10°) standard observer was used to calculate the whiteness index of the samples (Eq. (2)):

$$W = Y + 800(x_n - x) + 1700(y_n - y)$$
(2)

where w represents the whiteness index, Y is the Y-tristimulus value of the sample, x_n and y_n indicate the chromaticity coordinates of light sources used in CIE XYZ color space and x and y show similar values for the sample.

To calculate the chromaticity of the samples, their reflectance was measured using a SF-600 reflectance spectrophotometer (Datacolor, Switzerland). An average value of the five measured reflectances was used for the rest of the calculations.

H. Color Yield

Reflectance spectrums of the dyed samples were measured using a reflectance spectrophotometer (Ahiba AG CH-8305, Datacolor, Switzerland). Then the K/S value of the

Operation terms			
Desizing agent (w/v%)	Temperature (°C)	Time (min)	Sample code
Grey cotton	-	-	Grey cotton
α-amylase (0.1%)	80	45	α-amylase
[Mor-H]HSO ₄ (0.25%) pH: ~2.5	70	20	S1
		80	S2
	95	20	S3
		80	S4
[Mor-H]HSO ₄ (0.5%) pH: ~1.5	70	20	S5
		80	S6
	05	20	S 7
	95	80	S8

TABLE I

dyed samples was calculated using Kubelka-Munk formula (Eq. (3)):

$$K/S = (1-R)^2/2R$$
 (3)

In this equation, K and S represent absorption and scattering coefficient, respectively, and R is the reflectance of the sample. The value of the K/S of the dyed sample for the wavelength of minimum reflectance was considered as a measure of the color strength of the samples.

I. Color Fastness

Test method ISO 105-C01:1989 (E) was used to evaluate the color fastness of the dyed samples. According to this method, samples were stirred for 30 min in a bath containing 5 g/L of the detergent with a liquor to good ratio of 50:1 and at 40 °C. Then, the sample was washed and rinsed for 10 min and was dried under ambient temperature. Finally, the color fastness of the sample was assessed using an SDC Grey Scale according to ISO 105-A02:1993 (E) method.

III. RESULTS AND DISCUSSION

A. Optimum Condition of Desizing

Desizing process involves the treatment of fabric with the desizing agents to degrade or solubilize the sizing materials and remove the moieties from the surface of the product. It is impossible to completely dissolve starch in pure water and just a small amount of amylose with low molecular weight could be dissolved in its boiling point [26]. Therefore, efficient elimination of starch-based sizing materials via water is impossible. Considering this, it is necessary to utilize a desizing agent that contributes to the dissolving process or breakdown of the starch structure without

adverse effect on fabric strength. Traditionally, desizing was carried out by treating the fabric with enzymes, acids, and oxidizing agents. Herein, $[Mor-H]HSO_4$ as a mild noncorrosive acid has been used to catalyze the dissolving and breakdown of starch to short carbohydrates.

Try to find the optimum condition of desizing via [Mor-H]HSO₄ and compare the results with the common enzymatic method, samples were treated in different reaction temperatures, times, and concentrations of the ionic liquid (Table I). TEGEWA and weight loss of the treated samples with α -amylase and [Mor-H]HSO₄ have been shown in Table II. Results show that desizing via ionic liquid solutions can lead to desirable results (S3, S4, S7, and S8), achieving TEGEWA 6 or higher. None of the treated samples at 70 °C could reach proper TEGEWA. Accordingly, it seems that the temperature near to water boiling point is the most important prerequisite for a desirable desizing process by [Mor-H]HSO₄ solution. Samples S4 and S8 with TEGEWA 8-9 have proved that at 95 °C, it is possible to achieve the same quality as the enzymatic method.

To dissolve the starch size material, the ionic liquid should easily interact with starch polymer chains and destroy its intramolecular hydrogen bonds. The presence of [Mor-H]HSO₄ in combination with water can create appropriate conditions for high interaction between [Mor-H]HSO₄ and starch molecules. The water molecules can easily penetrate the starch structure and make it swollen; consequently, this swelling provides an easier path for the ionic liquid molecules to penetrate and destroy starch intramolecular hydrogen bonding [27]. In addition, the presence of water can reduce the viscosity of the solution, increase the diffusion coefficient and homogenize

TEGEWA AND WE	TABLE II TEGEWA AND WEIGHT LOSS OF THE DESIZED SAMPLES			
Sample	TEGEWA	Weight loss (%)		
Grey cotton	1	-		
α-amylase	8-9	8.39		
S 1	1	1.01		
S2	1-2	2.83		
83	6	5.01		
S4	8-9	8.22		
S5	2	2.93		
S 6	2	2.85		
S7	8	8.12		
S 8	8-9	8.31		

the whole system [28]. Therefore, it seems that water/ [Mor-H]HSO₄ combination is a suitable medium for dissolving and separating the starch granules from warp yarns of cotton; however, acidic characteristic of [Mor-H]HSO₄ may result in partial decomposition of starch structure [23].

Given that the size material is the major impurities of grey cotton, the weight loss of fabrics after desizing can be an indicator for determining the quality of desizing. As it can be seen from Table II, weight loss of the treated samples shows the same trend as TEGEWA results. More than 8% of the weight of S4, S7, S8, and their enzymatic desized counterpart were decreased (Table II) mainly due to the elimination of sizing materials.

Removal of impurities from the surface of desized samples via [Mor-H]HSO₄ is observable in the SEM images (Fig. 1). There are many adhering particles and debris on the surface of the grey cotton surface (Fig. 1a), which have almost disappeared after the desizing process and

the smooth surface of fibers has become visible (Fig. 1b). The particles on the surface of grey cotton could be related to the presence of size, waxes, proteins, etc. In addition, even after a high-quality desizing process, the existence of remnants of these impurities is inevitable. So other steps of cotton preparation like scouring and bleaching are crucial to remove the rest of the impurities effectively.

B. Concentration of Cationic Metals

Generally, demineralization of cotton fabrics is carried out using mineral acids like sulfuric acid and hydrochloric acid due to their capability to increase the solubility of cationic metals. [Mor-H]HSO₄ used in this research created a solution with a pH range from about 1.5 to 2.5. This acidic nature is expected to facilitate the elimination and hydrolysis of metal ion impurities from the textile substrate structure. Accordingly, there was an attempt to evaluate the effect of [Mor-H]HSO₄ in demineralization of the samples under the same condition applied for desizing. The results of these experiments are shown in Fig. 2, which indicates the concentration of some cationic metals on the desized samples.

As seen from the charts in Fig. 2, the concentration of Fe^{2+} , Cu^{2+} , Mg^{2+} , Ca^{2+} , Zn^{2+} , Na^+ , and K^+ cations on the desized samples via [Mor-H] HSO₄ are less than that on the enzymatic desized samples. Particularly differences in concentration of Fe^{2+} , Mg^{2+} , Ca^{2+} , and Zn^{2+} cations are more obvious. However, the differences of Na⁺ and K⁺ concentration among the samples are not noteworthy. In addition, the instrument could not detect Mn^{2+} cations in all samples. Also, results indicate that there is no sharp difference in concentrations of cationic metals among the samples which are treated with different concentrations of [Mor-H]HSO₄. Thus, the concentration of cationic metals

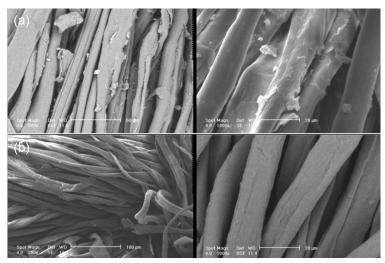


Fig. 1. SEM pictures of: (a) grey cotton and (b) desized sample via [Mor-H]HSO₄.

TABLE III

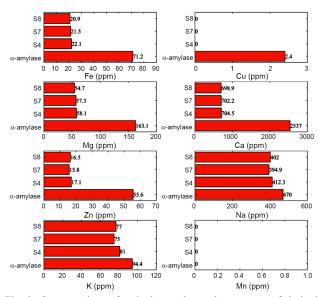


Fig. 2. Concentrations of cationic metals on the structure of desized samples.

with their negative aspects on the other wet processing could be significantly decreased through this novel starch desizing process. In other words, [Mor-H]HSO₄ not only could eliminate the sizing materials by destroying hydrogen bonds of starch structure but also could demineralize the substrate by increasing the solubility of cationic metals. Therefore, [Mor-H]HSO₄ provides the possibility of simultaneously desizing and demineralization of the cotton fabric.

C. Tensile Properties of Desized Samples

Generally, two main drawbacks of using mineral acids as a desizing or demineralization agent are their adverse effect on the strength of fabrics and being corrosive that could damage the body of desizing instruments. In fact, the similar structure of starch and cellulose makes it necessary to use a desizing agent with a specific reaction that saves the structure of cellulose intact. This is the reason why enzymatic desizing is so admirable. In this research, sulfuric acid is used to synthesize the [Mor-H]HSO₄, and this process could be carried out inside special resistant reactors. Therefore, in the process of desizing via [Mor-H]HSO₄, strong acids like sulfuric acid are not directly in touch with the fabric. Nevertheless, ILs like [Mor-H]HSO₄ are mild acids and it seems necessary to

TENSILE STRENGTH OF SAMPLES DESIZED VIA α -AMYLASE AND IONIC LIQUIDS 95% Confidence interval for mean Sample Tenacity (N/mm2) Lower bound Upper bound 59.87 56.35 63.38 α-amylase S158.14 54.21 62.06 S2 60.57 57.68 63.45 **S**3 59.90 55.33 64.46

57.81

52.02

55.12

53.51

55.59

64.64

62.05

61.93

59.66

65.14

61.23

57.04

58.53

56.59

60.37

S4

S5

S6

S7

S8

investigate its effect on the strength of samples. Therefore, the tenacity of the samples was measured and the average value of 20 measurements for each sample, beside 95% confidence interval and one-way ANOVA are shown in Tables III and IV, respectively. Results show that there is no statistically significant difference among the strength of samples (Tables III and IV, p-values=0.527>0.05). In contrast with mineral acids, while [Mor-H]HSO4 could be considered as a powerful desizing agent, it does not have a negative impact on the tensile properties of the final product. The reason for this phenomenon could be the lower swelling rate of cellulose in the presence of water than starch-based sizing materials. Accordingly, no change in the fabric strength could be related to the low rate of ionic liquid molecules penetration into the crystalline structure of cotton in comparison with starch.

One of the most problematic issues in acid desizing or demineralization of cotton fabric occurs during air drying of pre-impregnated fabric with the acidic solution. In these cases, the strength of fabric extremely decreases [8]. In order to evaluate the [Mor-H]HSO₄ in this circumstance, samples were impregnated with [Mor-H]HSO₄ solution. After drying at ambient temperature, their strength was measured and the results are shown in Fig. 3. It is evident from the chart that the strength of samples impregnated with the ionic liquid solutions and control sample did not show a statistically significant difference. Even in samples

TABLE IV ONE-WAY ANOVA OF TENSILE STRENGTH OF DESIZED SAMPLES

	Sum of squares	df	Mean square	F	P-value
Between groups	213.210	8	26.651	0.892	0.527
Within groups	2420.902	81	29.888		
Total	2634.112	89			

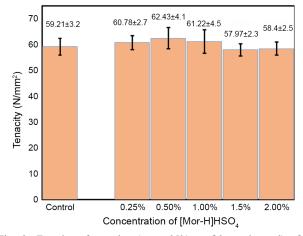


Fig. 3. Tenacity of samples (mean \pm 95% confidence interval) after pre impregnation with [Mor-H] HSO₄ solution and drying at ambient temperature.

that are treated with concentrations of $[Mor-H]HSO_4$ more than what is required for highly acceptable desizing, tenacity reduction did not happen. $[Mor-H]HSO_4$ is a mild acid compared to sulfuric acid and has no negative impact on the tenacity of samples. Furthermore, the large molecular size of $[Mor-H]HSO_4$ compared to sulfuric acid, which prevents easy penetration into cellulose's structure, could be another reason for this effectiveness difference.

D. Water Absorbency and Vertical Wicking of Desized Samples

In addition to the natural impurities, the presence of hydrophobic impurities in the film of sizing materials contributes to the hydrophobic properties of grey cotton. Accordingly, after removing the starch size, enhancement of water absorbency is expected. Wetting time and vertical wicking of desized samples are shown in Table V. The results indicate that even after a high-quality desizing via

TABLE V WETTING TIME AND VERTICAL WICKING OF DESIZED SAMPLES

Sample	Wetting time (s)	Vertical wicking (mm)			
Grey cotton	60+	0			
α-amylase	60+	6±3			
S1	60+	13±4			
S2	60+	16±3			
S3	15	42±5			
S4	0	59±4			
S5	60+	14±4			
S6	60+	10±5			
S7	0	62±3			
S8	0	57±5			

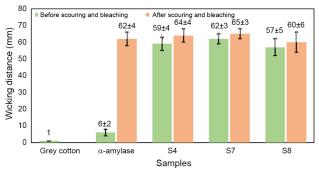


Fig. 4. Wicking distance (mean±95% confidence interval) of desized samples before and after scouring and bleaching.

 α -amylase (TEGEWA 8-9), the wetting time and vertical wicking distance of the enzymatic desized sample are lower than those of samples desized by the ionic liquid. Conventional enzymatic desizing cannot remove fatty and oily impurities from the cotton fabric [29]. Therefore, in spite of the elimination of size materials, wetting time and vertical wicking distance of enzymatic desized sample have not remarkably changed compared to grey cotton. On the contrary, wetting time in desized samples via [Mor-H]HSO₄ have decreased to about zero and vertical wicking distance was significantly increased (S4, S7, and S8). In addition to the elimination of size material, this decrease may be due to the hydrolysis of hydrophobic materials in the acidic condition of the ionic liquid solutions.

The results of the vertical wicking test before and after scouring and bleaching are shown in Fig. 4. The results show a considerable difference in the wicking distance of the enzymatic desized sample before and after the scouring and bleaching process. On the other hand, there is no statistically significant difference in the wicking distance of samples that are desized via [Mor-H]HSO₄ before and after desizing. Therefore it could be said that [Mor-H] HSO₄, in addition to the removing size material, is very effective in the elimination of other hydrophobic impurities during the desizing process.

E. Whiteness and Color Absorbency of Desized Samples

Generally, the main purpose of the preparation and pretreatment processes of a fabric is the removal of impurities and the quality of these processes guarantees and facilitates appropriate dyeing and other wet finishing steps. Accordingly, any fault in the desizing process could be observed as a defect in the dyeing process. Considering this point, the whiteness index of the grey cotton and desized samples with high TEGEWA (α -amylase, S4, S7, and S8) before and after the scouring and bleaching processes were measured (Table VI). Also, average K/S values of these samples at the wavelength of minimum reflectance

NO VIGAND COLOD FACTNESS OF THE DVFD SAMPLES

Sample Whiteness index	XX71 · / · · · · ·	Whiteness index (after scouring	After dyeing	
	and bleaching)	K/S (in 540 nm)	Color fastness	
Grey cotton	12.3	-	-	-
α-amylase	16.2	60.3	18.17	4
S4	15.8	60.0	17.19	4
S7	15.3	58.8	17.88	4
S 8	15.7	59.9	18.02	4

TABLE VI

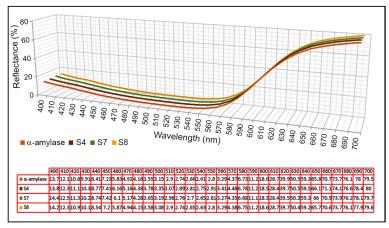


Fig. 5. Reflectance spectrum of the dyed samples via C.I. Direct Red 31 colorant.

(540 nm) plus the color fastness for each sample are shown in Table VI. The results in Table VI indicate that the whiteness of all samples is increased during the desizing process due to the elimination of the size and colored impurities. Also, it is shown that after the scouring and bleaching processes, the whiteness indexes of the samples desized via [Mor-H] HSO₄ solutions are close to the whiteness of the enzymatic desized sample. Therefore, differences in the witnesses could not lead to any possible differences in the dyeing results. The reflectance spectrums of dyed samples (Fig. 5) are very similar and there is no remarkable difference among them. The K/S of the desized samples via [Mor-H] HSO, is more or less the same as the corresponding value of the sample desized by the conventional enzymatic method. Similarly, the color fastness values are the same for all samples (Table VI). So, it is likely that using [Mor-H] HSO_4 for desizing does not have any adverse effect on the absorbency of direct dye on the samples, practically.

WILLTENEOG DIDEV OF DEGIZED GA

IV. CONCLUSION

This research focused on investigating the demineralization of cotton fabric using [Mor-H]HSO₄ and comparing this

simultaneous desizing/demineralization method with conventional acidic or enzymatic desizing methods. The results illustrated that desizing with 0.25% [Mor-H]HSO₄ solutions for 80 min and 0.5% [Mor-H]HSO₄ for 20 min at 95 °C could result in desizing with the same quality as enzymatic desizing (TEGEWA 8-9). Additionally, the concentration of cationic metals like Fe²⁺, Cu²⁺, Mg²⁺, Ca²⁺, and Zn²⁺ was dramatically decreased. This desizing/ demineralization method did not show any negative impact on the strength of fabrics and had a notable effect on increasing the water absorbency of the fabric.

Generally, this combined desizing/demineralization method makes it possible to achieve a high-quality starch desizing/demineralization and has some extra advantages compared to the enzymatic method, like long shelf-life and easy recoverability. In addition, being low cost and availability of the required reagents to synthesize [Mor-H]HSO₄ make this method proper for industrial production processes.

ACKNOWLEDGMENT

Financial support of the Isfahan university of technology (IUT) is gratefully appreciated.

REFERENCES

- M.J. Farrell, M.J. De Boskey, and M.A. Ankeny, "Improving the wettability of enzyme-bleached cotton fabric with inclusion of sodium surfactin", *ACS Sustain. Chem. Eng.*, vol. 4, no. 3, pp. 1569-1572, 2016.
- [2] P.J. Wakelyn, N.R. Bertoniere, A.D. French, D.P. Thibodeaux, B.A. Triplett, M.-A. Rousselle, W.R. Goynes Jr, J.V. Edwards, L. Hunter, and D.D. McAlister, *Cotton Fiber Chemistry and Technology*, 1st ed., CRC, 2006.
- [3] A. Rehman, Z.A. Raza, R. Masood, M.T. Hussain, and N. Ahmad, "Multi-response optimization in enzymatic desizing of cotton fabric under various chemo-physical conditions using a Taguchi approach", *Cellulose*, vol. 22, pp. 2107-2116, 2015.
- [4] L. Wang, Z.-Q. Xiang, Y.-L. Bai, and J.-J. Long, "A plasma aided process for grey cotton fabric pretreatment", *J. Clean. Prod.*, vol. 54, pp. 323-321, 2013.
- [5] M.A. Imran, T. Hussain, M.H. Memon, and M.M.A. Rehman, "Sustainable and economical one-step desizing, scouring and bleaching method for industrial scale pretreatment of woven fabrics", *J. Clean. Prod.*, vol. 108, pp. 494-502, 2015.
- [6] V.A. Dehabadi, K. Opwis, and J. Gutmann, "Combination of acid-demineralization and enzymatic desizing of cotton fabrics by using industrial acid stable glucoamylases and α-amylases", *Starch-Stärke*, vol. 63, no. 12, pp. 760-764, 2011.
- [7] A. Hebeish, M. Hashem, and A. Higazy, "A new method for preventing catalytic degradation of cotton cellulose by ferrous or ferric ions during bleaching with hydrogen peroxide", *Macromol. Chem. Physic.*, vol. 202, no. 6, pp. 949-955, 2001.
- [8] S.R. Karmakar, *Chemical Technology in the Pre-Treatment Processes of Textiles*, Elsevier, 1999.
- [9] C. Tomasino, *Chemistry and Technology of Fabric Preparation and Finishing*, North Carolina State University, North Carolina, 1992.
- [10] M.M. Hasan, F. Nabi, and R. Mahmud, "Benefits of enzymatic process in textile wet processing", *Int. J. Fiber Text. Res.*, vol. 5, no. 2, pp. 16-19, 2015.
- [11] N. Ul-Haq and H. Nasir, "Cleaner production technologies in desizing of cotton fabric", J. Text. Inst., vol. 103, no. 3, pp. 304-310, 2012.
- [12] M.K. Chimata, C.S. Chetty, and C. Suresh, "Fermentative production and thermostability characterization of α amylase from aspergillus species and its application potential evaluation in desizing of cotton cloth", *Biotech. Res. Int.*, vol. 2011, 2011.

- [13] S.Y. Hwang, K. Nakashima, N. Okai, F. Okazaki, M. Miyake, K. Harazono, C. Ogino, and A. Kondo, "Thermal stability and starch degradation profile of α-amylase from streptomyces avermitilis", *Biosci. Biotech. Biochem.*, vol. 77, no. 12, pp. 2449-2453, 2013.
- [14] A.H.M. Fauzi and N.A.S. Amin, "An overview of ionic liquids as solvents in biodiesel synthesis", *Renew. Sust. Energ. Rev.*, vol. 16, no. 8, pp. 5770-5786, 2012.
- [15] S. Mallakpour and Z. Rafiee, "Ionic liquids as environmentally friendly solvents in macromolecules chemistry and technology, part I", *J. Polym. Environ.*, vol. 19, pp. 447-484, 2011.
- [16] D.Z. Troter, Z.B. Todorović, D.R. Đokić-Stojanović, O.S. Stamenković, and V.B. Veljković, "Application of ionic liquids and deep eutectic solvents in biodiesel production: a review", *Renew. Sust. Energ. Rev.*, vol. 61, pp. 473-500, 2016.
- [17] A.R. Hajipour and F. Rafiee, "Acidic bronsted ionic liquids", Org. Prep. Proced. Int., vol. 42, no. 4, pp. 285-362, 2010.
- [18] M. Vafaeezadeh and H. Alinezhad, "Brønsted acidic ionic liquids: Green catalysts for essential organic reactions", J. Mol. Liq., vol. 218, pp. 95-105, 2016.
- [19] R.S. Balaskar, S.N. Gavade, M.S. Mane, M.S. Shingare, and D.V. Mane, "Morpholinium bisulfate [morH][HSO₄]-promoted O, S, and Nacylation at room temperature", *Green Chem. Lett. Rev.*, vol. 4, no. 1, pp. 91-95, 2011.
- [20] R.S. Balaskar, B.B. Shingate, M.S. Shingare, and D.V. Mane, "Morpholinium bisulfate [morH][HSO₄]: an efficient and reusable catalyst for the synthesis of bis(indolyl)methanes", *Arab. J. Chem.*, vol. 9, pp. S120-S123, 2016.
- [21] A.R. Hajipour and Z. Nasresfahani, "Mild and efficient chemoselective tetrahydropyranylation of alcohols using Brønsted acidic ionic liquid as catalyst under solvent-free conditions", *Synth. Commun.*, vol. 42, no. 13, pp. 1995-2006, 2012.
- [22] J. Rahmatinejad, A. Khoddami, A. Abdolmaleki, and H. Izadan, "Brønsted acidic ionic liquids: innovative starch desizing agents", *Carbohyd. Polym.*, vol. 157, pp. 468-475, 2017.
- [23] A. Abdolmaleki and Z. Mohamadi, "Acidic ionic liquids catalyst in homo and graft polymerization of ε-caprolactone", *Colloid Polym. Sci.*, vol. 291, pp. 1999-2005, 2013.
- [24] A. Abdolmaleki, Z. Mohamadi, B. Rezaei, and N. Askarpour, "Synthesis of small-band gap poly(3,4ethylenedioxythiophene methine)s using acidic ionic

liquids as catalyst", *Polym. Bull.*, vol. 70, pp. 665-679, 2013.

- [25] N. Chand, R.H. Sajedi, A.S. Nateri, K. Khajeh, and M. Rassa, "Fermentative desizing of cotton fabric using an α-amylase-producing Bacillus strain: Optimization of simultaneous enzyme production and desizing", *Proc. Biochem.*, vol. 49, no. 11, pp. 1884-1888, 2014.
- [26] A. Bertolini, *Starches: Characterization, Properties, and Applications*, CRC, 2009.
- [27] S. Mateyawa, D.F. Xie, R.W. Truss, P.J. Halley, T.M. Nicholson, J.L. Shamshina, R.D. Rogers, M.W. Boehm, and T. McNally, "Effect of the ionic liquid

1-ethyl-3-methylimidazolium acetate on the phase transition of starch: Dissolution or gelatinization?", *Carbohyd. Polym.*, vol. 94, no. 1, pp. 520-530, 2013.

- [28] W. Liu and T. Budtova, "Dissolution of unmodified waxy starch in ionic liquid and solution rheological properties", *Carbohyd. Polym.*, vol. 93, pp. 199-206, 2013.
- [29] C.-W. Kan, C.-F. Lam, C.-K. Chan, and S.-P. Ng, "Using atmospheric pressure plasma treatment for treating grey cotton fabric", *Carbohyd. Polym.*, vol. 102, pp. 167-173, 2014.