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Evaluation of chitosan based pretreatment for cotton and linen dyeing with direct dyes and reactive dyes

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ABSTRACT

*Cellulosic materials like cotton and linen are excellent textile substrates for dyeing with reactive and direct dyes. Due to their cellulosic nature, cotton and linen exhibit good affinity towards direct and reactive dyes. This good affinity is the reason for good washing and rubbing fastness. Chitosan is a bio-based polymer gained by the deacetylation of chitin. In contrast to cellulose, chitosan exhibits also amino functional groups. The purpose of this paper is to evaluate if a chitosan based pretreatment of cotton and linen can lead to different dyeing properties. After different chitosan based pretreatments, the color properties are determined by CIEL*a*b* indices. The rubbing fastness in dry and wet conditions is measured. Even if in the actual study no positive effects were determined by pretreatment of chitosan, the determined results could be utilized in future research to develop other functional treatments of cotton and linen materials with implemented chitosan.*

Keywords
cotton,
linen,
chitosan,
direct dyes,
reactive dyes,
rubbing fastness

1 Introduction

Cotton counts for around 20% of the world's fiber production and it is the most important natural fiber [1, 2]. Further, linen is an important bast fiber collected from the woody stalk of *Linum* [3]. Linen is smoother than cotton and possesses good heat conductivity, but linen fiber is somewhat compact and its dyeing is described to be more challenging compared to the dyeing of cotton [3]. Because of the dominant cellulose content in both fibers, different types of dyes are useful for the dyeing of cotton and linen [4]. Additionally, chitosan-containing recipes can be used for pretreatment purposes of fibers and by this influence dyeing procedures [5]. One suitable approach to achieve antimicrobial properties on textiles is the use of chitosan which is a natural polymer and therefore probably more biocompatible, not toxic, and less allergenic than other approaches [6, 7]. Other approaches for antimicrobial finishing are using metal ions or quaternary ammonium compounds [8–10]. Chitosan is prepared by deacetylation from chitin. Chitosan is a linear polysaccharide, which contains different amounts of β-(1 → 4)-linked 2-amino-2-deoxy-β-D-glucopyranose and 2-acetamido-2-deoxy-β-D-glucopyranose residues [6, 7, 11, 12]. With an increasing degree of deacetylation, the number of amino groups in the chitosan chemical structure increases. For comparison, Figure 1 shows the chemical structures of cellulose, chitin, and chitosan with a 100% deacetylation degree. Because of the presence of the amino group, chitosan is water soluble at acidic pH. Hosseinnejad and Jafari addressed that a lower pH and degree of chitosan acetylation favor the antimicrobial action of chitosan [13].

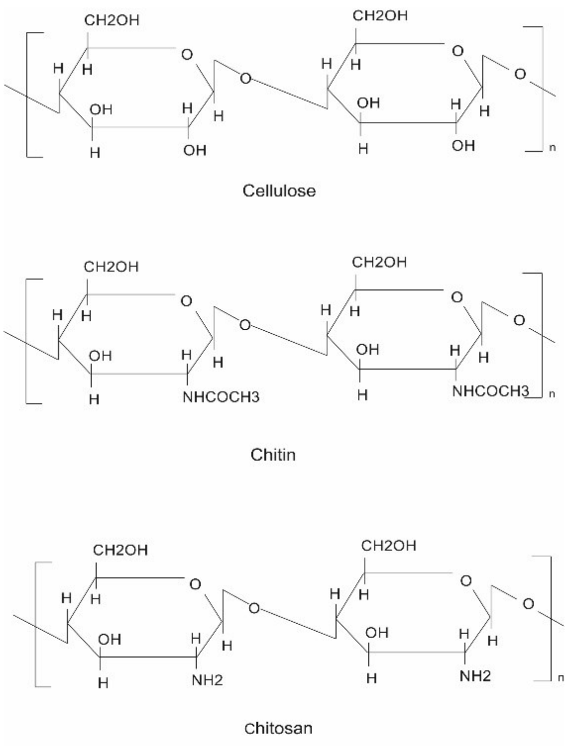

Fig. 1 Chemical structure and resemblance of cellulose, chitin, and chitosan.

Cellulosic materials like cotton and linen show a good affinity towards direct and reactive dyes due to the formation of hydrogen bridges, or covalent bonds respectively, with the cellulosic hydroxyl groups [14-17]. Physical adsorption of direct dye molecules onto cellulose fibers is an important factor, influencing the dyeing process with such dyes directly [18]. Due to the absence of reactive groups, direct dyes do not form covalent bonds with cellulose and exhibit weaker wash fastness [19, 20]. To improve the fastness properties of the direct dyes, cellulosic materials are treated with metal salts or extra auxiliary chemicals [21]. Since reactive dyeing is based on the formation of covalent bonds between the reactive group of the dye and the hydroxyl group of the cellulosic fiber, such processes lead to excellent wash fastness [22].

Currently, reactive dyes maintain the largest consumption in the world, but from the ecological point of view, reactive dyes are also part of a controversial discussion [21]. Zhang et al. presented chitosan application on cotton [23]. Reactive dyes are the most popular industrially applied dyes for dyeing cotton and for other natural fibers for their versatility and good wash fastness [24, 25]. There are also vat dyes (e.g. indigo) for the mass coloration of cotton [26]. However, the dyeability of linen is reported to be problematic in several applications [27]. The conventional way of dyeing the cotton with reactive dyes termed 'exhaust dyeing' contains two-stage processes: exhaustion and fixation [23]. The following aspects are mentioned for reactive dyes for dyeing cellulosic fibers- a variety of hues, good wash fastness, good light fastness, and high leveling properties [28]. The ability of reactive dyes to form covalent bonds to cellulosic hydroxyl groups should render them suitable to connect to the nucleophilic amine groups of chitosan too.

The two most common anchor systems in reactive dyes are related to the functional groups vinylsulfone and triazine. Commercial dyes can carry one or more of these anchor groups of one or both types. The BEZAKTIV GO dyes from CHT Germany are vinylsulfone dyes. Vinylsulfone groups react easily as Michael-Systems as shown in Figure 2. Because such Michael-Systems are highly reactive, these groups are usually protected with a pH-sensitive protection group like a sulfate. Triazine-based anchors often comprise a monochlorotriazine group, but also dichloro-, and even fluorotriazines are possible. These undergo a nucleophilic substitution reaction as in Figure 3. More electronegative leaving groups such as fluoro and a higher nucleophilic character of the attacking group [29, 30] usually increase the reaction speed. Therefore, the reaction rate can be increased at higher pH. It is therefore plausible that triazine-type anchors will also react similarly with amine groups although they are less nucleophilic than hydroxyl groups. Vinylsulfone groups are also reported to react with amine groups [31].

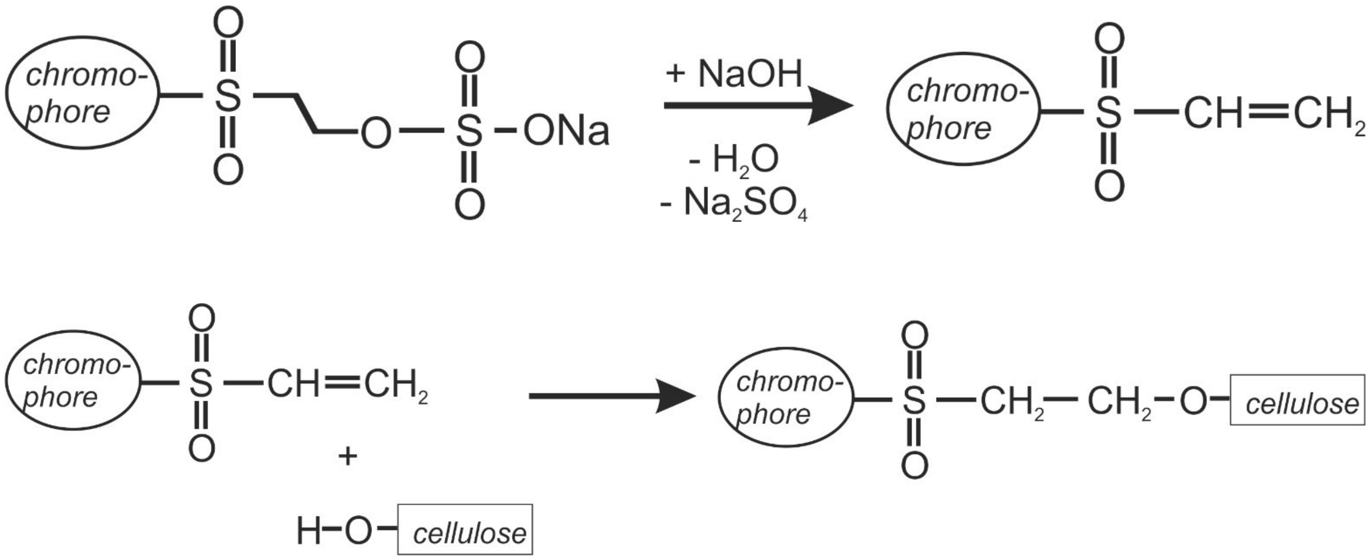

Fig. 2 Activation of protected vinylsulfone dye by alkaline treatment (top), Michael-Addition to cellulosic OH (bottom).

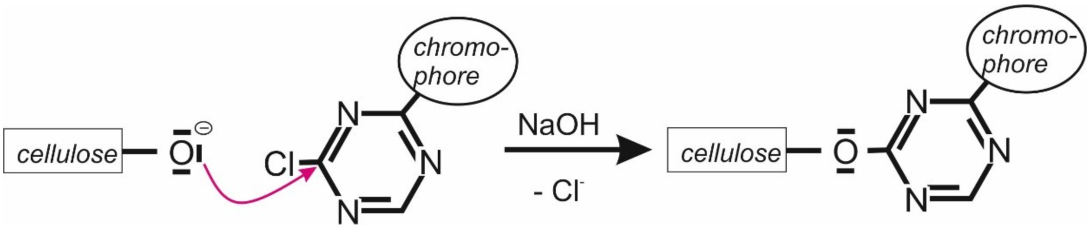

Fig. 3 Schematic view of the reaction of triazine anchor with the hydroxy group of cellulose

The actual study aims to evaluate if treatment with a chitosan-containing recipe can influence the dyeing properties of cotton and linen. For this, cotton and linen fabric samples are pretreated with a chitosan solution dissolved in 3% acetic acid followed by direct dyeing and reactive dyeing in an exhaust dyeing machine. Two direct dyes from the same supplier and two reactive dyes from the same supplier are applied on both cotton and linen specimens in different concentrations. Finally, the reached color properties and the rubbing fastness are determined.

2 Experimental section

2.1 Materials

Two different types of fabrics are used for dyeing experiments – cotton fabric and linen fabric. The weight per area of both fabrics is 200 g/m^2 and 126 g/m^2, respectively. The fabrics used in this study are purchased from the company Anita Pavani Stoffe OHG (Heuchelheim, Germany) and previously washed before further application. The microscopic images of used original cotton and linen fabrics are presented in Fig. 4.

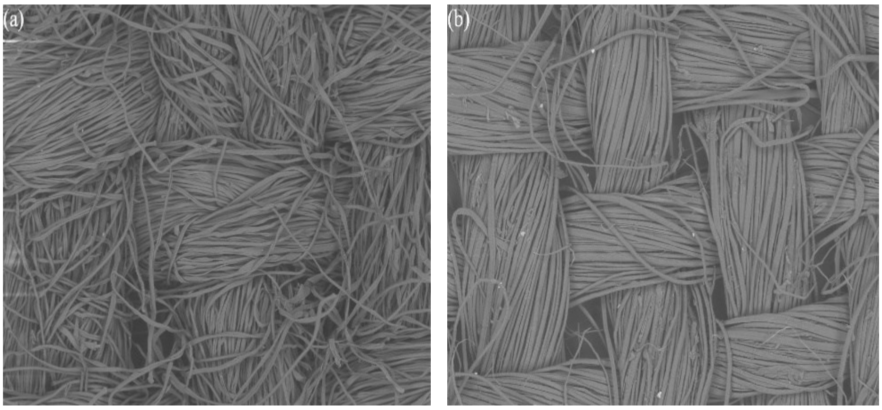

Fig. 4 SEM images of investigated fabrics. (a) Cotton, (b) Linen.

Chitosan, of brown color and a degree of deacetylation (DA) ≥ 85% was purchased from Carl Roth GmbH (Karlsruhe, Germany). The pretreatment procedure is carried out on a universal padding machine, DL-2500 HV from Feyen Maschinen GmbH (Krefeld, Germany).

Two different types of dyes with two distinct hues (blue and red) are applied to perform the dyeing procedure. The direct dyes used are SOLOPHENYL BLUE TLE and SOLOPHENYL RED 7BE from HUNTSMAN (Langweid, Germany). The reactive dyes used are BEZAKTIV GO BLUE and BEZAKTIV GO RED from CHT Germany GmbH (Tübingen, Germany). For the application of both dyes on cotton and linen, an exhaust dyeing machine Polycolor from Werner Mathis AG (Switzerland) is used. In addition, for reactive dyeing, a leveling agent SARABID MIP from CHT Germany GmbH (Tübingen, Germany) is applied along with soda ash, caustic soda, and sodium sulfate. A Mathis soapy machine (Switzerland) is used for after-treatment, and COTOBALANC SEL from CHT Germany GmbH (Tübingen, Germany) is added to the rinse water.

2.2 Pretreatment procedure

Pretreatment is applied to both cotton and linen fabric samples on a Horizontal & Vertical Type Padder Machine, DL-2500 HV (Feyen Maschinen GmbH, Krefeld). Each sample is padded twice with three different concentrations of chitosan, which are categorized into groups A (reference), B (with 0.5% implemented chitosan), and C (with 3% implemented chitosan). Table 1 illustrates the recipes of pretreatment solutions and the pick-up rate (%) by the samples.

The pick-up (%) of the used cotton and linen fabrics with implemented chitosan (0.5%, 3%) and for the reference sample is calculated as:

$$\text{Pick-up (\%)} = \frac{w - w_0}{w_0} \times 100\%$$

In this formula, w is the weight of the wet samples and w_0 is the weight of the original samples.

Table 1. Pick-up rate of cotton and linen with implemented chitosan. Given is the mass of fabric samples before and after the padding process (dry and wet mass).

Sample Group	Acetic acid (%)	Chitosan (%)	Cotton mass (g)	Cotton wet-pick-up	Linen mass (g)	Linen wet-pick-up
A	3	___	5.3 9.1	**72%**	3.1 4.8	**55%**
B	3	0.5	5.3 9.1	**72%**	3.1 4.8	**55%**
C	3	3	5.4 9.3	**72%**	2.9 4.5	**55%**

2.3 Direct dyeing of cotton and linen fabric

Pre-treated cotton and linen fabric samples are cut and weighed followed by dyeing in sealed stainless steel dye vessels. The dye vessels of the Polycolor dyeing machine contained the dye solution, prepared with various concentrations of auxiliaries. For dyeing, 5 g of cotton and 3 g of linen samples were used with a liquor ratio of 1:20. Both blue and red direct dyes are applied to three groups of samples of different chitosan content. Figure 5(a) shows the dyeing curve of direct dyeing for both cotton and linen samples. In this case, only sodium sulphate is applied as an exhausting agent with direct dyestuffs and soft water in a dye bath for both cotton and linen samples. Tables 2 and 3 show recipes for SOLOPHENYL blue and red shades respectively.

Table 2. Recipe realization of direct dye SOLOPHENYL BLUE TLE with different amounts and concentrations of other ingredients.

	Dye recipe no.	Sodium sulfate (g/L)	Direct dye (%)	Soft water (g)
COTTON	CO_1	3	0.1	92.0
	CO_2	6	0.3	79.0
	CO_3	7.5	0.5	67.5
LINEN	LI_1	3	0.1	55.2
	LI_2	6	0.3	47.4
	LI_3	7.5	0.5	40.5

Table 3. Recipe realization of direct dye SOLOPHENYL RED 7BE with different amounts and concentrations of other ingredients.

	Dye recipe no.	Sodium sulfate (g/L)	Direct dye (%)	Soft water (g)
COTTON	CO_4	7.5	0.5	87.5
	CO_5	12.5	1.0	77.5
	CO_6	20	2.0	60.0
LINEN	LI_4	7.5	0.5	52.5
	LI_5	12.5	1.0	46.5
	LI_6	20	2.0	36.0

2.4 Reactive dyeing of cotton and linen fabric

Both pretreated cotton and linen samples are dyed with BEZAKTIV GO BLUE and BEZAKTIV GO RED, using the exhaust process in a Zeltex Polycolor dyeing machine from Werner Mathis AG (Switzerland). The weight of samples and liquor ratio was kept similar as for direct dyeing. The leveling agent SARABID MIP from CHT Germany GmbH (Tübingen, Germany) is added to the dye bath. Figure 5(b) presents the dyeing curve of reactive dyeing with BEZAKTIV GO BLUE/RED for both cotton and linen samples. Tables 4 and 5 show recipes for dyeing with reactive dyes.

Table 1. Recipe realization of reactive dye BEZAKTIV GO BLUE with different amounts and concentrations of other ingredients.

	Dye recipe no.	Dye conc. (%)	Sodium sulfate (g/L)	Soda ash (g/L)	Caustic soda (g/L)	Leveling agent (g/L)	Soft water (g)
COTTON	CO_7	0.5	40	3.3	1.3	1.5	54.0
	CO_8	1.5	60	3.3	2.2	1.5	36.1
	CO_9	3.0	80	3.3	2.6	1.5	16.2
LINEN	LI_7	0.5	40	3.3	1.3	1.5	32.4
	LI_8	1.5	60	3.3	2.2	1.5	21.6
	LI_9	3.0	80	3.3	2.6	1.5	9.7

Table 2. Recipe realization of reactive dye BEZAKTIV GO RED with different amounts and concentrations of other ingredients.

	Dye recipe no.	Dye conc. (%)	Sodium sulfate (g/L)	Soda ash (g/L)	Caustic soda (g/L)	Leveling agent (g/L)	Soft water (g)
COTTON	CO_10	0.5	40	3.3	1.3	1.5	54.0
	CO_11	1.5	60	3.3	2.2	1.5	36.1
	CO_12	3.0	80	3.3	2.6	1.5	16.2
LINEN	LI_10	0.5	40	3.3	1.3	1.5	32.4
	LI_11	1.5	60	3.3	2.2	1.5	21.6
	LI_12	3.0	80	3.3	2.6	1.5	9.7

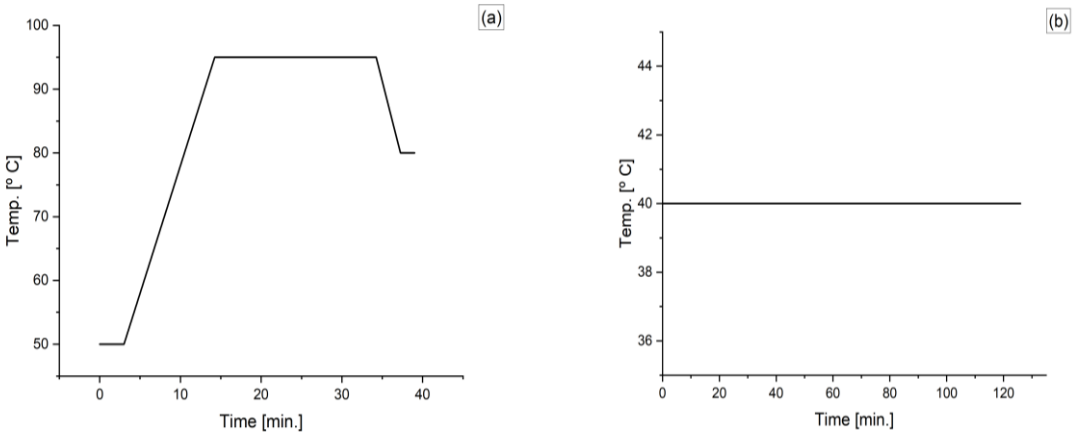

Fig. 5 Dyeing process curve- (a) direct dyeing, (b) reactive dyeing.

2.5 After-treatment

Dyed cotton and linen samples were processed in the Mathis soapy machine for the after-treatment. The after-treatment process was conducted at 40º C by adding 1.5 g/L COTOBALANC SEL to the rinse water. To adjust the pH value, an appropriate amount of acetic acid was added to the process. Finally, the samples were spin-dried.

2.6 Analytical methods

For the evaluation of the dyeing results of both cotton and linen samples, the CIEL*a*b* indices are determined. Color measurement is performed with a DATA Color 400 colorimeter (Rotkreuz, Switzerland). The fastness to rubbing is determined using a crock meter according to ISO 150 X-12. The wet and dry specimens of both cotton and linen are rubbed against a dry rubbing and wet rubbing cloth respectively. A grey scale is used to determine the staining of the rubbed samples. The microscopic images presented in Figure 4 are recorded with a scanning electron microscope (SEM) Tabletop TM3000 (Hitachi, Japan).

3 Results and Discussions

3.1 Color properties

To evaluate the color properties after dyeing, the dyed fabrics are documented by photographs, and the coloration results are evaluated by determining the CIE L*a*b* indices. The samples in group A (without implemented chitosan) are used as references and samples in groups B and C are compared with those in group A. Group B stands for a pretreatment with a 0.5% chitosan recipe and group C stands for a pretreatment with a 3 % chitosan recipe. Figure 6 shows the results for the cotton fabrics, while Figure 8 presents the results for linen fabrics dyed with 0.5% direct dye (SOLOPHENYL BLUE TLE) and 3% reactive dye (BEZAKTIV GO BLUE). Similarly, Figures 10 and 12 show the results for both cotton and linen fabrics dyed with 2% direct dye (SOLOPHENYL RED 7BE) and 3% reactive dye (BEZAKTIV GO RED).

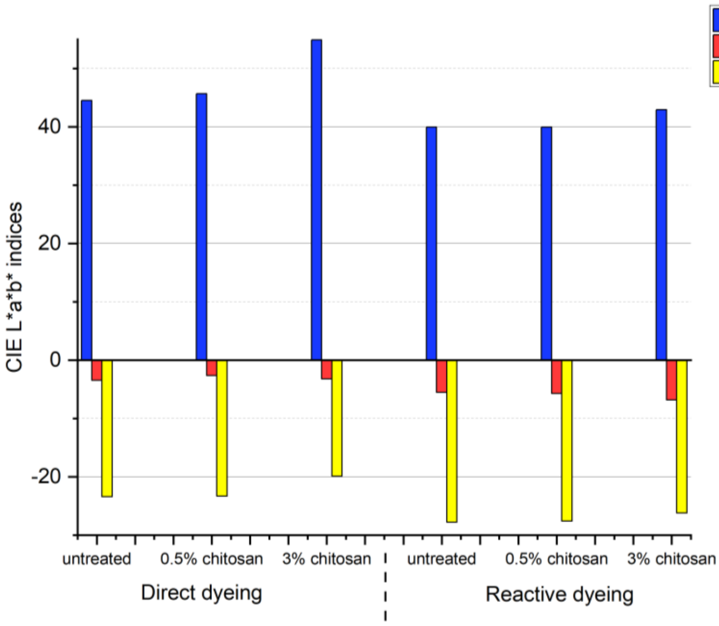

*Fig. 6 CIE L*a*b* indices of cotton fabrics dyed with 0.5% direct (SOLOPHENYL BLUE TLE) and 3% reactive (BEZAKTIV GO BLUE) dyestuffs.*

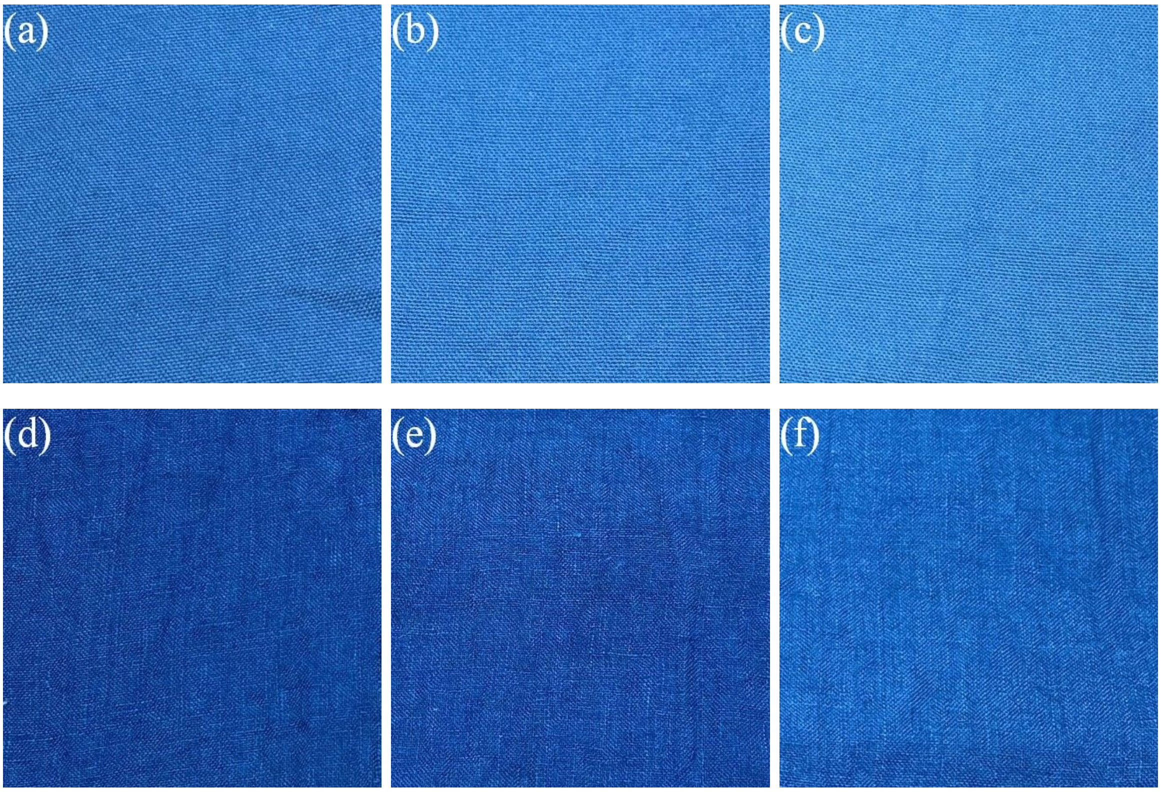

Fig. 7 Results of reactive dyed cotton and linen samples with 3% BEZAKTIV GO BLUE - (a) reference cotton w/o chitosan, (b) 0.5% chitosan, (c) 3% chitosan, (d) reference linen w/o chitosan, (e) 0.5% chitosan, (f) 3% chitosan.

For both cotton and linen fabrics (Figures 7 and 9) dyed with direct and reactive blue dyes, Figures 6 and 8 present significant decreases in values of coordinates a* and b*. In addition, reactive dyed linen fabrics show negative values of a*, although negative values of b* are almost identical for both blue direct and reactive dyestuffs (Figure 8). From the rectangular coordinate system, it is clear that for blue dyes brightness is increased, and slight decrease in a*, which appears green, and a decrease in b*, which appears bluish. These results of CIE L*a*b* indices are in good accordance with the color impression of the samples documented by the photographs. It can be concluded that for these dyestuffs the chitosan pretreatment leads to a weaker coloration, which could be caused by lower dye uptake or decreased dye affinity to the fiber. One explanation for lower dye uptake could be the coverage of porous areas of the fiber by the chitosan layer and by this hinders the dye to penetrate the main body of the fiber. In addition, it is reported that treatments with chitosan-containing recipes can decrease the hydrophilicity of cotton [32]. A less hydrophilic fiber could also show a weaker uptake of dye.

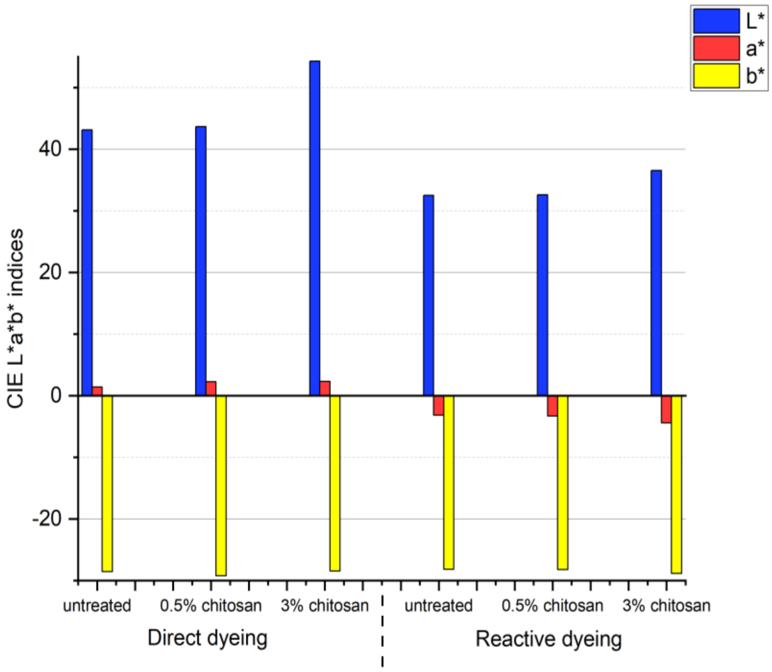

*Fig. 8 CIE L*a*b* indices of linen fabrics dyed with 0.5% direct (SOLOPHENYL BLUE TLE) and 3% reactive (BEZAKTIV GO BLUE) dyestuffs.*

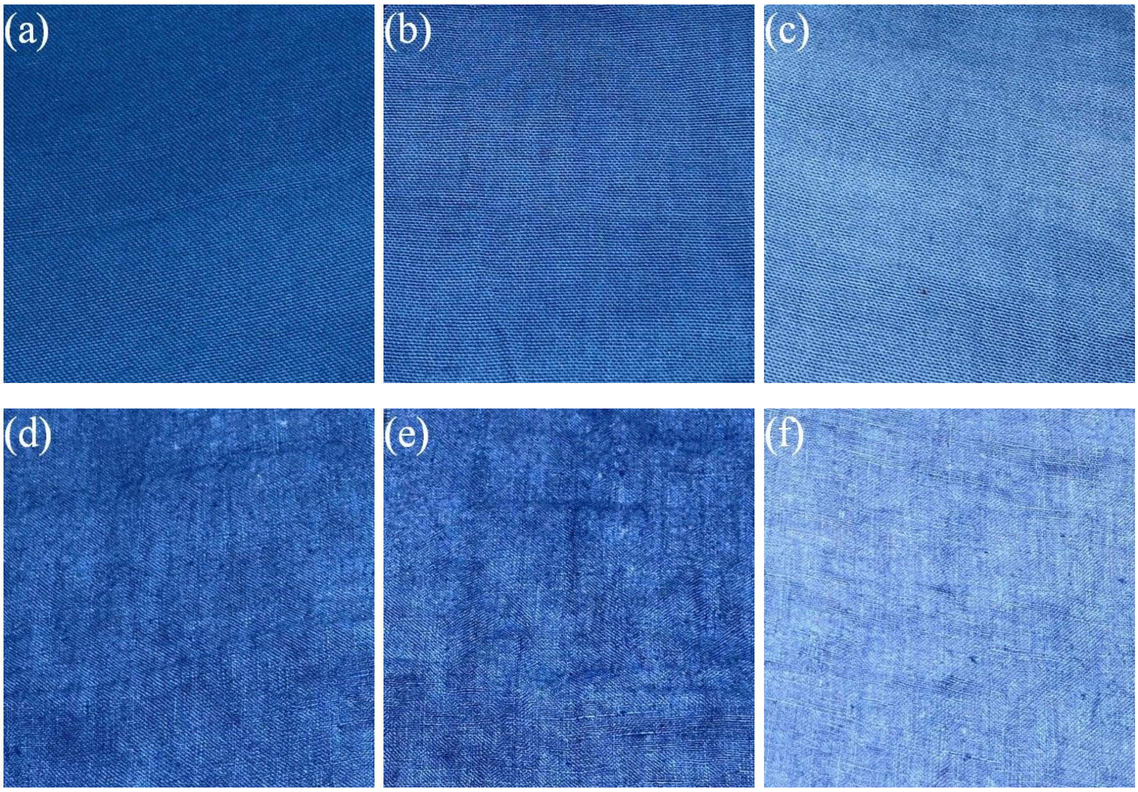

Fig. 9 Results of direct dyed cotton and linen samples with 0.5% SOLOPHENYL BLUE - (a) reference cotton w/o chitosan, (b) 0.5% chitosan, (c) 3% chitosan, (d) reference linen w/o chitosan, (e) 0.5% chitosan, (f) 3% chitosan.

Figures 10 and 12 present the results for cotton and linen fabrics dyed with 2% direct dye (SOLOPHENYL RED 7BE) and 3% reactive dye (BEZAKTIV GO RED). The coordinate L* represents the brightness of the fiber material and darker coloration appears with decreasing value of L*. The coordinate a* shows a color shift from red to green and the decrease in red coloration follows the decrease in a*. The coordinate b* indicates a color shift from yellow to blue and the decrease in yellow follows the decrease in b* and appears bluer. In contrast, for both cotton and linen fabrics (Figures 11 and 13) dyed with direct and reactive red dyes, Figures 10 and 12 arguably significant increase in values of coordinate a*.

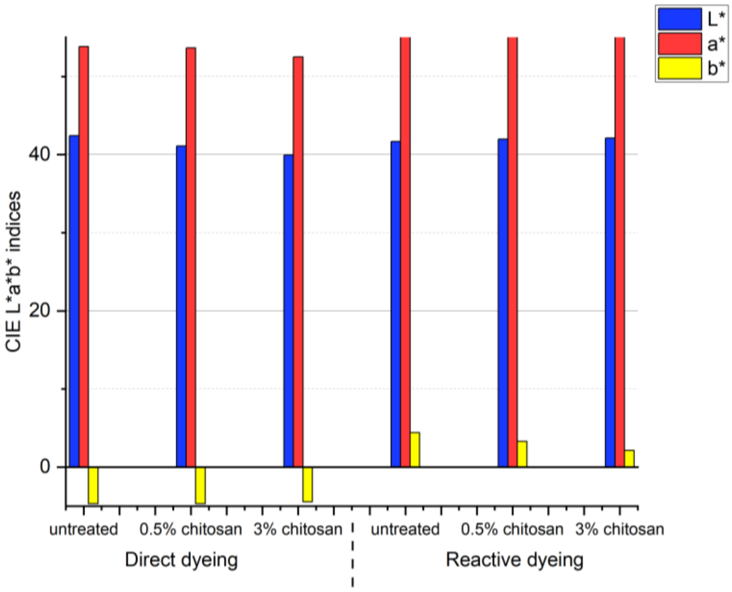

*Fig. 10 CIE L*a*b* indices of cotton fabrics dyed with 2% direct (SOLOPHENYL RED 7BE) and 3% reactive (BEZAKTIV GO RED) dyestuffs*

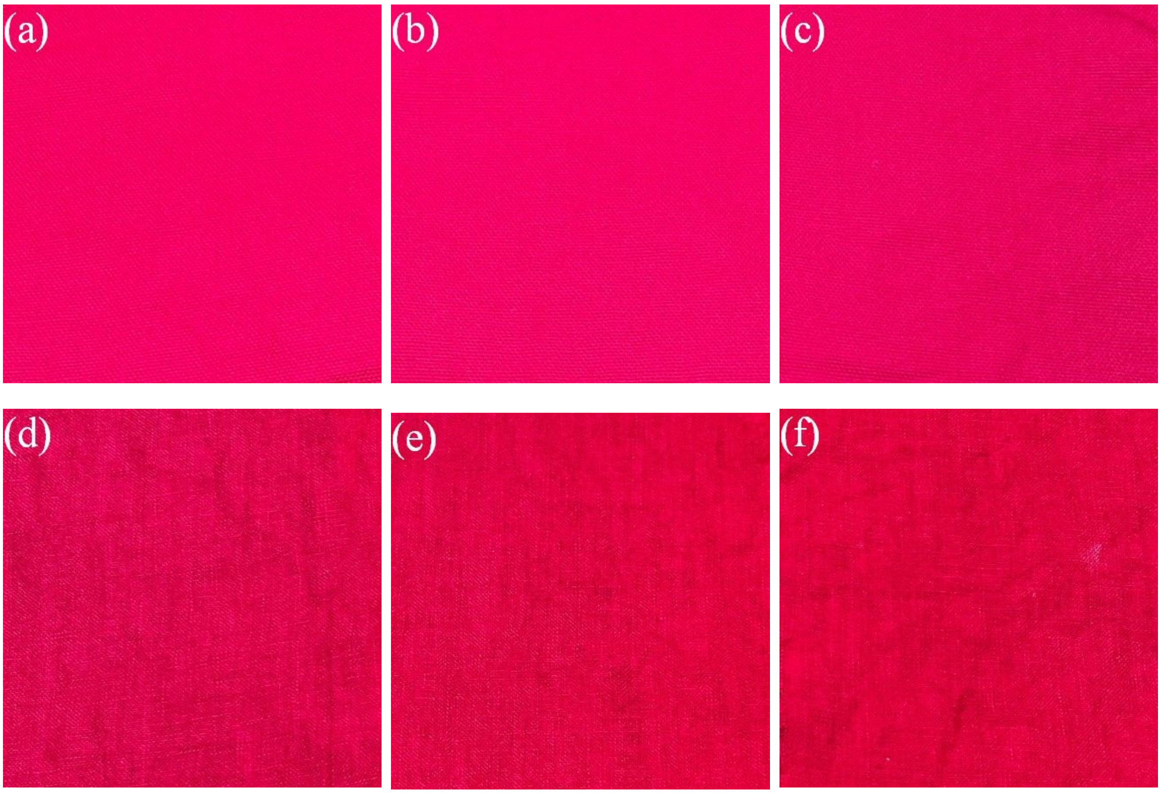

Fig. 11 Results of reactive dyed cotton and linen samples with 3% BEZAKTIV GO RED - (a) reference cotton w/o chitosan, (b) 0.5% chitosan, (c) 3% chitosan, (d) reference linen w/o chitosan, (e) 0.5% chitosan, (f) 3% chitosan.

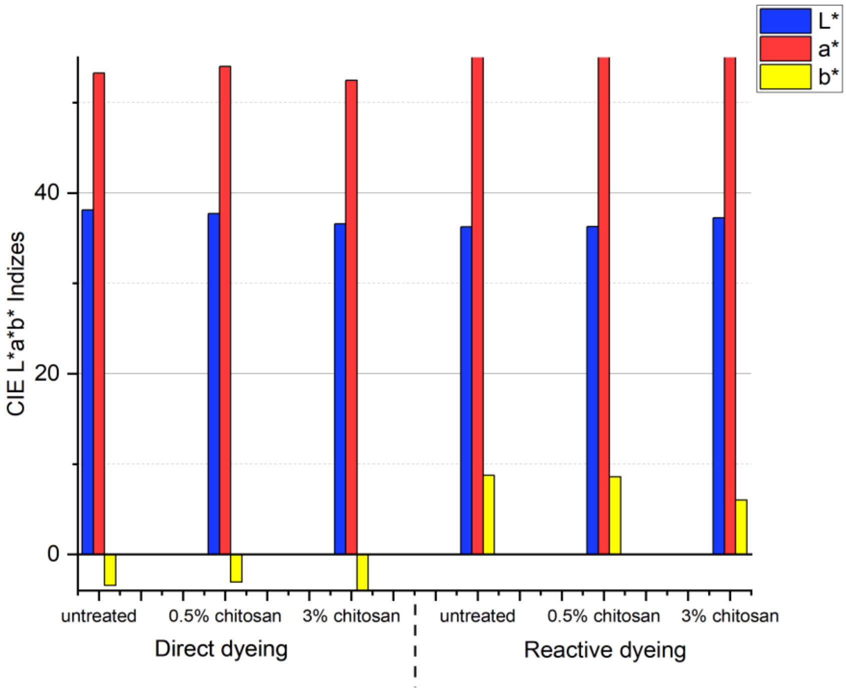

*Fig. 12 CIE L*a*b* indices of linen fabrics dyed with 2% direct (SOLOPHENYL RED 7BE) and 3% reactive (BEZAKTIV GO RED) dyestuffs*

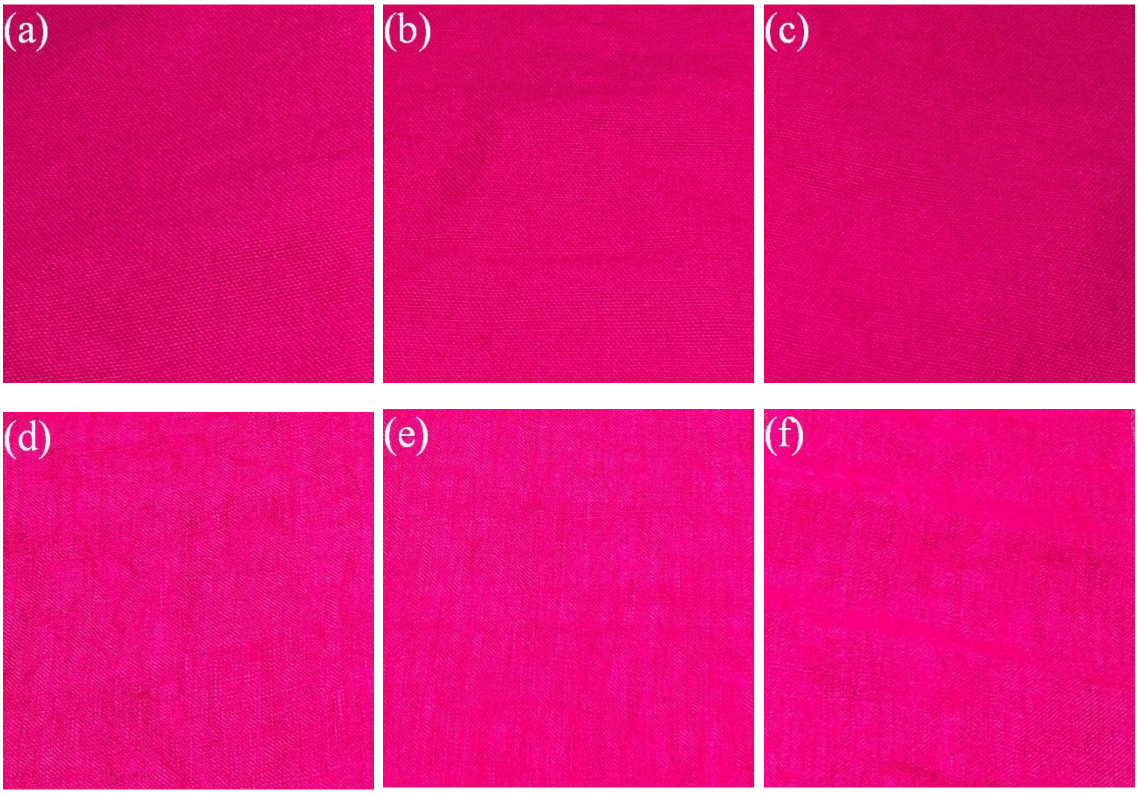

Fig. 13 Results of direct dyed cotton and linen samples with 2% SOLOPHENYL RED 7BE - (a) reference cotton w/o chitosan, (b) 0.5% chitosan, (c) 3% chitosan, (d) reference linen w/o chitosan, (e) 0.5% chitosan, (f) 3% chitosan.

However, reactive dyed both cotton and linen fabrics show an increase in coordinate b*, although fabrics dyed with direct dyes indicate a decrease in coordinate b*. The gain of coloration from direct dyes is slight, certainly due to fewer reactive groups present or bonded together in the structure.

It can be concluded that the influence of chitosan pretreatment of the dyeing with the investigated two red dyestuffs is small. It cannot be stated that the chitosan treatment leads to a more intensive coloration or dye uptake. This is the main difference between the investigated two blue dyestuffs, which exhibit weaker dyeing results after chitosan pretreatment. Here, it can be only estimated that the type of chromophore structure responsible for the coloration of dye molecule has a different affinity to chitosan-treated fabrics. Current investigations show that pretreatment with chitosan recipes offers no improvement in dyeing properties.

3.2 Rubbing fastness

The rubbing fastness for both dry and wet conditions is performed to determine the fixation of the dyes onto the specimens. A gray scale is used to evaluate the grade of rubbing fastness in the range of 1 to 5, where grade 5 indicates the best result. The grading system shows color transfer from the dyed cotton and linen samples to a white cotton fabric which they are rubbed against. Grade 5 represents no color transfer, while grade 1 represents a strong color transfer to the cotton sample. Generally, wet rubbing fastness is determined by rubbing against a wet cotton sample, which leads to a lower grading value. Tables 6 and 7 illustrate the grading value for both cotton and linen fabrics respectively in dry and wet conditions.

From the fastness grading results, it can be seen that samples dyed with reactive dyes (BEZAKTIV BLUE/RED) exhibit relatively good fastness to rubbing than those dyed with direct dyes (SOLOPHENYL BLUE/RED). Due to the anchor groups of reactive dyes, they are prone to form covalent bonds, which makes the dyes difficult to rub off from the surface of the samples. In contrast, direct dyes having no anchor groups can only form disperse or polar interactions with chitosan and/or the cellulose, thus exhibiting a weaker fixation compared to reactive dyes. As expected, the wet rubbing fastness is weaker than the dry rubbing fastness for both cotton and linen fabrics. The pretreatment with chitosan does not improve the rubbing fastness and especially the applied direct dyes gain lower rubbing fastness by the application of chitosan. If the chitosan layer closes the porous structures of the natural fiber substrates, especially the application of direct dyes can be affected. As these dyes are not penetrating the fiber well, they are more exposed to rubbing on the fiber surface. Due to the good fixation of reactive dyes, the rubbing effect is less significant on the fabrics compared to direct dyeing.

Table 6. Rubbing fastness of cotton fabrics dyed with reactive and direct dyes (pretreated with 3% acetic acid for Group A, B, and C).

Dye type (Reactive/Direct)	**Dye conc. (%)**	**Group A (Reference)**		**Group B (0.5% Chitosan)**		**Group C (3% Chitosan)**	
		Dry	***Wet***	***Dry***	***Wet***	***Dry***	***Wet***
BEZAKTIV GO BLUE	0.5	5	4-5	4-5	4-5	4-5	4-5
	1.5	5	4	4-5	4	4-5	3
	3.0	4-5	4	4-5	3-4	4-5	3-4
BEZAKTIV GO RED	0.5	4-5	4	4-5	3-4	4-5	3
	1.5	4-5	3	4-5	2-3	4-5	2-3
	3.0	4	2	4	2	4-5	2
SOLOPHENYL BLUE TLE	0.1	5	4	4	3	4	3
	0.3	4	4	3-4	3	4	3
	0.5	4	4	3-4	2-3	4	3
SOLOPHENYL RED 7BE	0.1	4-5	3	3-4	2	3	1-2
	0.3	4	3-4	3-4	2	2-3	1-2
	0.5	4	2-3	3	2	3	1-2

Table 7. *Rubbing fastness of linen fabrics dyed with direct and reactive dyes (pretreated with 3% acetic acid for Group A, B, and C).*

Dye type (Reactive/Direct)	**Dye conc. (%)**	**Group A (Reference)**		**Group B (0.5% chitosan)**		**Group C (3% chitosan)**	
		Dry	***Wet***	***Dry***	***Wet***	***Dry***	***Wet***
BEZAKTIV GO BLUE	0.5	5	4-5	4-5	4-5	4-5	4
	1.5	4-5	4	4-5	4	4-5	3-4
	3.0	4-5	3	4-5	3	4-5	3
BEZAKTIV GO RED	0.5	4-5	2-3	4-5	2-3	4-5	2-3
	1.5	4	2-3	4	2-3	4	2
	3.0	3-4	2	3-4	2	3-4	1-2
SOLOPHENYL BLUE TLE	0.1	4	2-3	4	2-3	4	3
	0.3	4	2-3	4	2	4	2
	0.5	4	2	3-4	1-2	4	2
SOLOPHENYL RED 7BE	0.1	4-5	2-3	4-5	2	3-4	1-2
	0.3	4-5	2	4-5	2	4	1-2
	0.5	4-5	2	4-5	2	3	1-2

4 Conclusions

Dyeing recipes for cotton and linen fabrics with pre-treated chitosan are presented. Four different dyes are investigated – two direct dyes and two reactive dyes. Given the dyeing results, it can be stated that by pretreatment of fabrics, the dyeing properties cannot be improved. In certain cases, even less dye uptake with finally lower coloration was gained as a function of increased chitosan application. In addition, the rubbing fastness is not positively influenced by chitosan pretreatment. One possible explanation for these results could be the closure of porous structures on the fiber surface by the applied chitosan layer, which hindered the dye penetration deeply into the body of the fiber. Even in the actual study, no positive effects were determined by the pretreatment of chitosan; although the determined results might be utilized in future research to develop other functional treatments of cotton and linen materials with implemented chitosan.

Author Contributions

The presented results are part of the master thesis of Tian Benrui performed at the Hochschule Niederrhein (Faculty of Textile and Clothing Technology) in the year 2022. Boris Mahltig acted as the supervisor, and Thomas Grethe acted as the second supervisor for the master thesis. Mohammad Toufiqul Hoque assisted in the research and wrote the current article.

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Conflicts of Interest

The authors declare no conflict of interest.

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