Decolorization properties and mechanism of reactive-dyed cotton fabrics with different structures utilized to prepare cotton pulp

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Abstract

It is critical to develop the mild decolorization technology to accomplish clean pulping in order to overcome the issues caused by the high consumption of energy and severe degradation of cellulose during the preparation of cotton pulp from waste cotton textiles. Discarded cotton fabrics was treated using a technique named as the sodium hydroxide-sodium dithionite system to remove color. During the procedure, the function of decolorization parameters, the effect of decolorization treatment on the structure and properties of cotton fabrics, and mild decolorization mechanism were investigated according to the different chromogenic systems and active groups of reactive dyes, especially. The findings demonstrate that NaOH can hydrolyzes covalent bonds between dye and cotton fiber and $Na_2S_2O_4$ destroys chromophores to achieve decolorization. The chemical makeup and crystal structures of cotton cellulose are barely affected throughout the decolorization process. It is worth noting that the strength of the decolored cotton fabric can be retained by more than 90%, thus not affecting the subsequent pulping requirements.

Introduction

The textile industry has developed to be one of the largest and oldest industries in the world (Kasavan et al. 2021). With the growth of the world's population, so does the need for textile products (Islam and Bhat 2019; Shirvanimoghaddam et al. 2020; To et al. 2019). Nevertheless, as global textile output rises, the textile industry faces significant challenges. The usage cycle of textiles is shrinking as living conditions rise and consumer habits change (Athanasopoulos and Zabaniotou 2022; Lopatina et al. 2021). Millions of tons of clothes and textiles are discarded or incinerated each year, causing resource waste and serious environmental pollution(Jiang et al. 2022; Pensupa et al. 2017; Sharma et al. 2020). Cotton fabrics in waste textiles account for a sizable amount of waste textiles, and the supply of cotton fibers has always been limited by the "the contradiction between food and cotton" (Dahlbo et al. 2017; Leal et al. 2019). Therefore, by recycling of cotton fabrics, both economic and environmental benefits may be accomplished.

The majority of current technologies for recycling waste cotton fabrics rely on physical process that combine the waste material with high-quality cotton fiber to create yarns via disassembly and loosening (Cao et al. 2022; Ribul et al. 2021). The resultant textiles are of low grade, poor quality, and restricted in color and design. By converting waste cotton fabric into spinning pulp, it's possible to realize the high-value utilization of waste cotton fabric, minimize resource waste and the environment pollution, and resolve the contradiction between the supply and demand of textile fiber (Lu et al. 2022; Wang et al. 2021). The issue of mild decolorization must be addressed first before the preparation of dissolving pulp using waste cotton fabrics. In theory, the conventional color decolorization approaches for textiles are mainly divided into two categories based on the effects of decolorizing treatment on dye molecules in the substrate matrix. One method is known as destructive decolorization, in which the shades on the substrates were stripped using a serious of chemical reactions to decompose the chromophores of dye molecules (He et al. 2019; Long et al. 2017). The other is to achieve the goal of decolorization via desorption, in which the dye molecules are desorbed from the colored substrates by various solvents and/or surfactants without disintegration of the dye chromophores disintegrating (He et al. 2019; Long et al. 2017). Furthermore, destructive decolorization is the most popular and often utilized technique in practical manufacturing. One of the categories is reductive decolorization, which is decolorized primarily by the use of reducing agents such as sodium dithionite and thiourea dioxide. Such procedures have minimal effect on the strength and molecular weight of the fabrics (He et al. 2021; Uddin et al. 2015), And this method is not conducive to pulping. The other type of decolorization is oxidative decolorization, which is accomplished by adding oxidants such as sodium hypochlorite, chlorine dioxide, ozone, and hydrogen peroxide. However, this approach has a significant influence on the strength and molecular weight of the fabrics(Li et al. 2022). To summarize, considering the varying molecular weight degradation degrees of waste cotton fabrics with complicated origins and variable colors, it is preferable to utilize reducing agents for decolorization.

The $NaOH/Na_2S_2O_4$ system has been widely used for decolorization of cotton fabrics dyed with reactive dyes. Currently, all of the necessary chemicals are added to the decolorization system to decolorize the dyed cotton fabric for the reductive decolorization. As a result, it is unclear which reagent (NaOH? or $Na_2S_2O_4$? or a combination of NaOH and $Na_2S_2O_4$?) was used as a decolorization agent for reactive dyes with distinct chromophores. Thus, we investigated the reductive decolorization of cotton textiles dyed with azo-, anthraquinone-, and azo-/anthraquinone- reactive dyes in this study. This study gives theoretical reference for the decolorization of reactive-colored cotton fabric, which is important for the recycling and usage of waste cotton fabric.

Experimental

Materials

A well-pretreated cotton fabric (CM120/2*CM120/2*150*80*57/58) was supplied by Lu Tai Group Co., Ltd. (Shandong of China) in this work. A commercial Reactive Red X-3B (C.I. Red 2; CAS: 17804-49-8), Reactive Blue KN-R (Reactive Blue 19; CAS:2580-78-1), and Reactive Red KE-3B (C.I. Reactive Red 120; CAS: 61951-82-4) were purchased from Longsheng Group Co., Ltd. (Zhejiang of China) and their chemical structures were depicted in Fig. 1. Sodium dithionite and sodium hydroxide were provided in an analytical reagent grade by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Coloration of the cotton substrate with Reactive Red X-3B, Reactive Blue KN-R, Reactive Red KE-3B The reactive dye (4.0%, o.m.f) was dissolved in deionized water with a bath ratio of 1:50, and the prepared cotton fabric sample was dipped into the dyeing bath to begin the dyeing process. The other dyeing procedures were performed in accordance with the process curves shown in **Fig. 2** and the dyeing recipe shown in Table 1.

Table 1
Coloration recipe for cotton fabric samples with reactive dye

Composition of dyeing bath	Dosages		
	Red X-3B dye	Blue KN-R dye	Red KE-3B dye
Reactive dye	4.0%, o.m.f	4.0%, o.m.f	4.0%, o.m.f
NaCl	30 g/L	60 g/L	60 g/L
Na_2CO_3	15 g/L	30 g/L	30 g/L
Soap	5 g/L	5 g/L	5 g/L

Decolorization Of Cotton Substrate Dyed With Reactive Dyes

According to a predefined request, cotton fabrics dyed with different reactive dyes were decolored carried out in a $NaOH/Na_2S_2O_4$ system with a bath ratio of 1:20. After the reaction, the decolorized cotton fabric was thoroughly washed with deionized water till neutral and dried at a temperature of 60 °C.

Characterization

Lightness values

The color intensity value (K/S value) and the lightness value on the colored and decolorized cotton fabric were determined using a Datacolor 850 instrument (Datacolor. Co., Ltd., USA) a equipped with simulated D_{65} light source lamp and 10° visual angle at a maximum characteristic absorption wavenumber (λ_{max}) for an individual reactive dye. And a 4-folded form for each colored and decolorized cotton fabric sample and eight-site detections on the individual sample were used for the duration of the shade determination. Then an arithmetic mean of the achieved lightness values for an individual sample was calculated according to Eq. (1).

$$L = \frac{1}{n}\sum_{i=1}^{n} L_i$$

1

Super Depth Of Field Microscope

Paraffin was first melted and smeared to the surface of the dyed and discolored cotton fabrics to prepare the samples. The super depth of field microscope (DVM6M, Leica Co., Ltd., Germany) was used to investigate the decolorization on cotton fabric samples under different conditions in the $NaOH/Na_2S_2O_4$ system, according to the surface and section morphological changes of cotton fabric samples.

Ft-ir Analysis

Chemical structures of all samples were examined using an FT-IR instrument (Nicolet iS50, Thermo electron Co., Ltd., US). The cotton fabrics samples before and after decolorization were dried and crushed into a homogenous powder. The sample powder (2 mg) was combined with IR-grade KBr (200 mg), and pellets were prepared on a KBr press for testing. The FT-IR spectra for the samples were detected from 500.0 cm^{-1} to 4000.0 cm^{-1} with a resolution of 4.0 cm^{-1} at ambient conditions.

Wide-angle X-ray Diffraction Analysis

A X-ray diffractometer (Smartlab SE, Rigaku Corporation Co., Ltd., Japan) was employed to analyze the crystal structures of cotton fabrics before and after decolorization. The cotton fabric samples were dried and crushed into a homogenous powder for testing using a 40.0 kV tube voltage and a 40.0 mA tube current. The X-ray diffraction patterns were recorded in the range of $2\theta = 5\tilde{4}5^{\circ}$.

Breaking Strength

The breaking strength of cotton fabric samples colored and decolorized was determined using an Universal Material Testing Machine (INSTRON5967, Instron Co., Ltd., USA) using the strip method of China textile criteria of GB/T3923.1 -2013. The strip of the cotton fabric samples for determination was cut to a dimension of 5.0 cm × 25.0 cm in both warp and weft directions. The breaking strength of each cotton fabric sample was an average result of three replicate determinations.

Results And Discussion

Effect for decolorization of cotton fabrics with different reactive dyes by NaOH independently

The proposed method's decolorization mechanism on reactive-dyed cotton fabric substrate with different chromophores at different dyed-cotton treated by different concentrations separately of sodium hydroxide solution in the $NaOH/Na_2S_2O_4$ system was investigated using the K/S value of decolorized cotton fabrics with the bath ratio of 1:20 at different temperatures for 80.0 min duration. Figure 3 depicts the K/S value curves of several decolorized cotton materials at the boiling temperature.

Figure 3 shows that when sodium hydroxide was employed to treat colored cotton fabrics separately, the K/S values of the decolorized cotton fabrics declined steadily as the dose was increased. And neither the maximum absorption wavelength nor the absorption peak has altered. At the same time, the hue of the decolorizing solution darkened. The results shows that the covalent bond between dye and cotton fiber was hydrolyzed, allowing the hydrolyzed dye to be transferred from cotton fabrics to the decolorizing solution; additionally, the chromophore of the dye was not destroyed when sodium hydroxide was used to treat dyed cotton fabrics individually.

The lightness value could be calculated to judge the effect of sodium hydroxide on decolorization for cotton fabrics. Figure 4 depicts the findings that the influence of sodium hydroxide concentration on the lightness of cotton fabric at different temperatures. Figure 4 clearly shows that increasing the dose of sodium hydroxide and the temperature enhanced the lightness value. However, after treating Reactive Red X-3B colored cotton fabric with a solution of 70 g/L sodium hydroxide at the boiling temperature, the result of decolorization was unsatisfactory, with the lightness value of just 58.13, as shown in Fig. 4a. Because of the relatively lively active group of Reactive Red X-3B, it was easy to react with cotton fabric to form covalent bonds, the decolorization result was not optimal when sodium hydroxide was simply used to decolorized Reactive Red X-3B colored cotton fabrics. As demonstrated in Fig. 4b, the impact of decolorization with varied doses of sodium hydroxide at the boiling temperature for Reactive Blue KN-R colored cotton fibers was outstanding. The lightness value of Reactive Blue KN-R colored cotton fabric could achieve 62.83 treated with a solution of 10 g/L sodium hydroxide. The lightness value improved to 71.67 when the sodium hydroxide concentration increased to 30 g/L. It may be concluded that the decolorization result was outstanding when sodium hydroxide was simply administered to decolorize Reactive Blue KN-R colored cotton fibers because the covalent connections between Reactive Blue KN-R and cotton fabric were not stable under alkaline circumstances. Decolorization was accomplished with the solution of 70 g/L sodium hydroxide at the boiling temperature, as shown in Fig. 4c, with a lightness value of around 63.70 for Reactive Red KE-3B colored cotton fabric. It can be inferred that the decolorization effect was common when sodium hydroxide was simply applied to decolorize Reactive Red KE-3B dyed cotton fabrics because it was also relatively easy to react with cotton fabric to form covalent bonds due to Reactive Red KE-3B's relatively lively active group. And the strength of covalent bond between dye and cotton fiber for Reactive Red KE-3B colored cotton fabrics is between that of other two reactive dyes.

Effect For Decolorization Of Cotton Fabrics With Different Reactive Dyes By Naso Independently

The proposed method's decolorization mechanism on reactive-dyed cotton fabric substrate with different chromophores at different dyed-cotton treated by different concentrations separately of sodium dithionite solution in the NaOH/$Na_2S_2O_4$ system was investigated using the K/S value of decolorized cotton fabrics with the bath ratio of 1:20 at different temperatures for 80.0 min duration. Figure 5 depicts the K/S value curves of several decolorized cotton materials at the boiling temperature.

Figure 5a and 5c reveal that when sodium dithionite was used to treat Reactive Red X-3B and Reactive Red KE-3B colored cotton fabrics separately, the K/S values of the decolorized cotton fabrics, especially which at the maximum absorption wavelength, declined rapidly with increasing sodium dithionite dose. No new absorption peak was formed, and the decolorization solution was very light in color. The results demonstrate that sodium dithionite immediately reacted with dyes in cotton fabrics, reducing the chromophore -N = N- in the dye to -NH-NH-, resulting in cotton fabric decolorization. Among them, the maximum absorption wavelength did not change treated with 0.8 g/L sodium dithionite at the boiling temperature.

To assess the influence of sodium dithionite on decolorization, the lightness value might be determined. Figure 6a depicts the corresponding findings that the influence of sodium hydroxide concentration on the lightness of cotton fabric at different temperatures. It demonstrates that when colored cotton fabric was treated with 0.2 g/L sodium dithionite solution at the boiling temperature, the lightness value was as high as 78.73. The lightness value of cotton fabrics improved to 84.46 when the sodium dithionite concentration reached 0.6 g/L. However, no additional significant improvement was obtained with a sodium dithionite dose greater than 0.6 g/L. Because the reducing ability of sodium dithionite to the Reactive Red X-3B chromophore was extremely targeted, it may be concluded that sodium dithionite might be utilized to decolorize cotton fabrics without utilizing sodium hydroxide. Moreover, the high lightness of cotton fabrics can be made with only a small amount of dithionite, which may be due to the fact that the chromophore of Reactive Red X-3B is mono azo and the reactive group is very active. As a result, a dose range of 0.4 to 0.6 g/L of the reducing agent sodium dithionite was indicated for the decolorized of the reactive-dyed cotton substrate using the proposed approach and the $NaOH/Na_2S_2O_4$ combination.

Surprisingly, the color of Reactive Red KE-3B colored cotton fibers after decolorization was a little yellow after treated with 4.0 g/L sodium dithionite at the boiling temperature, despite the fact that no new absorption peak was formed. Therefore, the decolorization effect of Reactive Red KE-3B dyed cotton fabric is characterized by the lightness value. Figure 6c depicts the similar findings. At the same temperature, the lightness values increased as the sodium dithionite concentration increased. Despite the fact that the Reactive Red KE-3B colored cotton fabric was treated with 4.0 g/L sodium dithionite at the boiling temperature, the lightness values were only 64.62. As a result, sodium dithionite alone had a poor decolorization effect on colored cotton fibers. In terms of the sodium hydroxide decolorization study in Fig. 5c and the sodium dithionite decolorization analysis in **Fig. 6c**, it is obvious that solely utilizing sodium hydroxide for decolorization was unsuitable for Reactive Red KE-3B colored cotton fabrics. Because of the dis azo structure of Reactive Red KE-3B, sodium hydroxide and sodium dithionite should be used combined to treat colored cotton fabrics for a better decolorization effect. Additionally, despite the chromophores of both dye have been more thoroughly destroyed, the color of the cotton fabric is a little yellow as shortwave below 400nm is insensitive to the reductive destruction of sodium dithionite.

Figure 5b shows that when sodium dithionite was used to treat Reactive Blue KN-R colored cotton fibers separately, the maximum absorption wavelength of the dye on the decolorized cotton fabric changed from 600 nm to 480 nm with increasing concentration. This phenomenon varied significantly from sodium dithionite's decolorization of other colored cotton materials, indicating that it had different reduction capacities and reduction functions on different chromophores. Reactive Red X-3B has a mono azo structure, Reactive Red KE-3B has a dis azo structure, and Reactive Blue KN-R has an anthraquinone structure. The K/S value of the decolorized cotton fibers at 600 nm reduced dramatically as the concentration of sodium dithionite increased, but the K/S value at 480 nm increased. As a result, the lightness values were employed to quantify the decolorization effect of sodium dithionite on the Reactive Blue KN-R colored cotton fabric. **Figure 6b** depicts the similar findings, it demonstrates that the presence of sodium dithionite alone did not assist in decolorization since lightness values increased and then decreased as sodium dithionite concentration increased. Because of the increase reduction potential of the Reactive Blue KN-R chromophore, the effect of decolorization treatment of cotton fabric simply with sodium dithionite was not desirable. As a result, the Reactive Blue KN-R colored cotton fabrics should be decolorized using sodium hydroxide at a concentration of 30 g/L sodium dithionite.

Synergistic Effect Of Sodium Hydroxide And Sodium Dithionite For Reactive Red Ke-3b Dyed Cotton Fabrics

To investigate the synergistic effect of sodium hydroxide and sodium dithionite, the decolorization performance of the proposed method on the Reactive Red KE-3B cotton substrate was investigated using lightness values with a dose of 60 g/L sodium hydroxide and bath ratio of 1:20 at a temperature of 80.0 °C for 80.0 min duration. The results are depicted in Fig. 7.

Figure 7 shows that the suggested approach accomplished good decolorization performances, as characterized by lightness values, on the reactive-dyed cotton substrate at the most of the sodium dithionite dose. With an increase in sodium dithionite concentration, the lightness values increased dramatically from 55.85 to 76.67. The rate of lightness value improvement from 55.85 to 69.68 was very rapid with sodium dithionite dosages ranging from 0 to 1 g/L. The lightness values improved from 73.23 to 76.68 as the amount of reducing agent increased from 2 to 5 g/L. Despite the fact that the lightness values approached 70, the dose of sodium dithionite did not rise much. It is suspected that adding sodium dithionite to sodium hydroxide solution might boost the decolorization impact greatly. As a result, a concentration range of 2 to 4 g/L for the reducing agent sodium dithionite was suggested in order to obtain a greater decolorization effect. The decolorization performance on the Reactive Red KE-3B cotton substrate was then tested further with a dose of 2 g/L sodium dithionite under the same conditions as the rest of the parameters. The results are depicted in Fig. 8.

Figure 8 shows that the speed of lightness value improvement from 63.48 to 70.30 was fast with the dose of sodium hydroxide from 10 to 40 g/L evidently. However, as an amount of sodium hydroxide was involved from 40 to 60 g/L, the lightness values were improved from 70.30 to 72.85, all exceeding 70, which could achieve a great decolorization effect. It can be inferred that adding sodium hydroxide to sodium dithionite solution could significantly improve the decolorization effect. Hence, a concentration range for sodium hydroxide from 40 to 60 g/L was recommended in order to obtain a greater decolorization effect.

Moreover, the decolorization mechanism of the $NaOH/Na_2S_2O_4$ system for the reactive-dyed cotton substrate involving various active species generation, transmission, attack, etc., is further summarized and described in Eqs. (2)−(4) (El-Sakhawy 2005; Malkavaara et al. 2000).

$$S_2O_4{}^{2-} + 2H_2O \rightarrow 2HSO_3{}^{-} + 2\left[H\right] + 2e^{-}$$

2

$$S_2O_4{}^{2-} + 2H_2O \rightarrow 2S_2O_6{}^{2-} + 4\left[H\right] + 4e^{-}$$

3

$$S_2O_4{}^{2-} + 3H_2O \rightarrow HSO_3{}^{-} + HSO_4{}^{-}4\left[H\right] + 4e^{-}$$

4

Effect For Decolorization Of Cotton Fabrics With Different Reactive Dyes At A Different Temperature

The proposed method's decolorization mechanism on reactive-dyed cotton fabric substrate with chromophores at different dyed-cotton treated with the bath ratio of 1:20 for 80.0 min duration at different temperatures in the NaOH/$Na_2S_2O_4$ system was further investigated. Among them, the Reactive Red X-3B cotton substrate was treated with a dose of 0.6 g/L sodium dithionite and the Reactive Blue KN-R cotton substrate was treated with a dose of 30 g/L sodium hydroxide. As well as the decolorization performance at a different temperature on the Reactive Red KE-3B cotton substrate was further investigated with a dose of 40 g/L sodium hydroxide, 2 g/L sodium dithionite. And all the results are respectively depicted in Fig. 9a **– 9c**.

Figure 9 reveals that the decolorization effect on cotton fabric with different chromophores was all very sensitive to the change in temperature. The lightness value was improved with increasing the temperature on cotton fabric with different chromophores. Generally, a suitable temperature is helpful to initiate the decomposition of the reducing agent of sodium dithionite in the aqueous solution to produce various active and powerful species for stripping the dye molecules. In addition, an appropriate increase in the temperature of the NaOH/$Na_2S_2O_4$ system is useful to speed up the different reaction rates and the diffusion of the active species in the substrate fibers, etc.

Figure 9a shows that the decolorization performance at different temperatures on Reactive Red X-3B dyed cotton substrate. It shows that an evident enhancement in the lightness value from 73.63 to 79.80 was observed as the temperature increased from 50 to 70 °C, accompanied with no further improvement as the temperature continues to rise due to a saturation of the produced powerful species on the cotton, or the deactivation of these active species at an overhigh temperature, as well as fewer dye molecules remained on the cotton, etc (He et al. 2019). It can be inferred that the higher the temperature was, the better the decolorization effect was, however, when the temperature was too high, the decomposition of sodium dithionite was also enhanced. The two effects existed at the same time, resulting in that the decolorization effect not significantly improved with increasing the temperature. Consequently, the temperature of decolorization about 70 °C was preferred for the proposed method on Reactive Red X-3B dyed cotton substrate by considering both the satisfactory performances of the decolorization efficiency and energy saving.

Figure 9b and Fig. 9c respectively show that the decolorization performance at a different temperature on Reactive Blue KN-R dyed cotton and Reactive Red KE-3B dyed cotton substrate. Similar analysis results in that the temperature of decolorization about 80 ℃ was preferred for both Reactive Blue KN-R dyed cotton fabric and Reactive Red KE-3B dyed cotton fabric.

Effect For Decolorization Of Cotton Fabrics With Different Reactive Dyes At Different Durations

Based on the above investigations, the decolorization performance of the proposed method at different durations was also explored in the $NaOH/Na_2S_2O_4$ system with a dose of 0.6 g/L sodium dithionite at a temperature of 70 ℃ for Reactive Red X-3B dyed cotton fabric. And for Reactive Blue KN-R dyed cotton fabric, the decolorization effect at different durations was explored with a dose of 30 g/L sodium hydroxide at a temperature of 80 ℃. For Reactive Red KE-3B dyed cotton fabric, the decolorization effect at different durations was explored with a dose of 40 g/L sodium hydroxide, 2 g/L sodium dithionite at a temperature of 80 ℃. The results are respectively shown in Fig. 10a-10c.

Figure 10 clearly demonstrates that the decolorization effect of cotton fabric increased gradually with the extension of decolorization durations. The influence of decolorization time on the decolorization effect of cotton fabric can be divided into two stages. Theoretically, a longer duration readily results in more decomposition of the reducing agent to produce more active and powerful species in the $NaOH/Na_2S_2O_4$ system for the decolorization of reactive dyes fixed on the substrate (He et al. 2019; Xie et al. 2017). Figure 10a shows that the enhancement for the lightness value from 76.85 to 78.32 on the Reactive Red X-3B dyed cotton substrate was observed as the duration from 5 min to 10 min. Then a continuous slow improvement was also obtained as the duration extended to 30 min, with the lightness value promoted to 81.16. Undoubtedly, all these powerful species and their efficient actions promoted the significant improvement of the lightness value as the increase of decolorization duration from 5 min to 10 min. However, the slow improvement of the lightness value with a further prolonged duration to 20 min was probably due to the slow diffusion of those active and powerful species into the inner phase of the solid fiber substrate for further decomposition of the fixed reactive dyes in which. Additionally, the no further improvement in the lightness value with the duration longer than 20 min was probably attributed to a saturation of the active species on the substrate, especially for them on the surfaces of the solid fibers, as well as due to the less remained and hard being decomposed dye molecules. Consequently, it is obvious that the decolorization duration with a range from 5 min to 10 min was preferred for the proposed method on Reactive Red X-3B dyed cotton substrate by taking into account both the satisfactory performances of the decolorization efficiency and energy saving.

Figure 10b and Fig. 10c respectively show that the decolorization performance at a different duration on Reactive Blue KN-R dyed cotton and Reactive Red KE-3B dyed cotton substrate. Similar analysis results in that the duration of decolorization about a range from 40 min to 60 min was preferred for Reactive Blue

KN-R dyed cotton fabric and which about a range from 50 min to 60 min was preferred for Reactive Red KE-3B dyed cotton fabric.

Investigation Of The Decolorization On Cotton Fabric With Super Depth Of Field Microscope Analysis

The samples of different dyed cotton fabrics decolorized under the optimal process were analyzed by super depth of field microscope, and the morphology of the surface and cross-sectional was observed. The results are shown in **Fig. 11**.

Figure 11 shows that reactive dyes of three different types of chromophores were uniformly distributed on the surface of the yarn and the cotton fiber wrapped inside the yarn before decolorization. And the color of different decolorized cotton fabrics was all white. There was nearly no dye on the cotton fabrics.

It can be inferred that the reactive dye on the fabric could be reduced by sodium dithionite and the mono azo chromophore of the dye could be destroyed for Reactive Red X-3B in **Fig. 11(1)**. It can be inferred that the reactive dye was promoted by sodium hydroxide to diffuse from the fabric into the solution through breaking the covalent bond between the dye and cotton fibers for Reactive Blue KN-R in **Fig. 11(2)**. It can be inferred that the reactive dye was promoted by sodium hydroxide to diffuse from the fabric into the solution through breaking the covalent bond between the dye and cotton fibers, and sodium dithionite to destroy the dis azo chromophore for Reactive Red KE-3B in **Fig. 11(3)**. Figure 11 clearly demonstrates that the dye could be stripped from cotton fabric and the excellent decolorization effect could be obtained for cotton fabrics dyed with three dyes of different chromophores in the $NaOH/Na_2S_2O_4$ system.

Investigation Of The Decolorization On Cotton Substrate With Mechanical Properties Analysis

From the above analysis, it can be seen that the dyes on cotton fabrics are basically removed, but its strength needs to be explored. If the strength of the cotton fabric decreases significantly after decolorization, it indicates that the cellulose molecular chain is broken and the molecular weight decreases, which affects the molecular weight regulation of subsequent pulping. The breaking strength of cotton fabric before decolorization and after the best decolorization process is shown in Fig. 12.

Figure 12 shows that the breaking strength of cotton fabrics decreased less after decolorization. Among which, the retention efficiency of warp breaking strength and weft breaking strength was 94.52% and 92.30%, 89.80% and 88.90%, 93.33% and 91.46% for Reactive Red X-3B, Reactive Blue KN-R and Reactive Red KE-3B dyed cotton fabrics, which was caused by the partial breakage of cotton fiber molecular chain during the decolorization process. This result is consistent with the slight decrease of the crystallinity of cotton fiber. Therefore, the physical and chemical structures of cotton cellulose were less affected because of various physical and chemical effects on the reactive dyes of cotton fabrics in the process of decolorizing cotton fabrics under atmospheric pressure and high temperature, the decolorization treatment of cotton fabrics with the NaOH/$Na_2S_2O_4$ system could achieve the effect of mild decolorization on waste cotton fabrics without affecting subsequent pulping.

Investigation Of The Decolorization On Cotton Substrate With Ft-ir Spectra Analysis

The above results highlight the possibility that the fixed reactive dye on cotton substrates could be removed via decolorization of the NaOH/$Na_2S_2O_4$ system. Therefore, to explore more information about decolorization reactions that occurred on the substrate and different dyed cotton substrates after decolorization at different decolorization conditions were investigated by employing FT-IR analysis. The recorded FT-IR spectra are depicted in Fig. 13.

Figure 13 reveals that some evident variations in the FT-IR spectra of the cotton substrates after decolorization at different decolorization conditions were observed in comparison with the reactive-dyed one. As for the sample of cotton substrate, the strong and typical absorption band at 3351.2 cm^{-1} mainly consisted of the combined stretching vibrations of O-H (v_{O-H}) from the macro chains of cotton as well as N-H (v_{N-H}) from the dye molecules, and the absorption bands at 2897.6 cm^{-1}, 2856.1 cm^{-1} were assigned to the asymmetrical and symmetrical stretching vibrations of C-H in -CH_2- groups, respectively (Choe et al. 2019; Chung et al. 2004). In addition, the absorption bands at 1061.6 cm^{-1} and 1029.8 cm^{-1} were assigned to stretch vibration absorption peaks of covalent bond C-O-R formed between dye molecules and cotton cellulose molecules and C-H in-plane bending vibration absorption peaks in cellulose molecular structure, and both absorption peaks are weak. The absorption peak heights at the two places were consistent in the infrared spectrum for the cotton fabric before dying in Fig. 13. However, the absorption peak at 1061.6 cm^{-1} was only slightly higher than the absorption peak at 1029.8 cm^{-1} in the infrared spectrum of different dyed cotton fabric due to the formation of covalent bonds between the dye and the fiber. And the intensities of these two absorption peaks did not change compared with those of Reactive dye X-3B dyed cotton fabrics (**Curve 2**). However, Reactive Blue KN-R dyed cotton fiber decolorized by sodium hydroxide (**Curve 4**), especially Reactive Red KE-3B dyed cotton fiber decolorized by sodium hydroxide/sodium dithionite (**Curve 6**), the absorption peak at 1061.6 cm^{-1} was significantly weakened. It can be inferred that the covalent bond formed by the dye and cotton cellulose was hydrolyzed and broken under the action of sodium hydroxide and it was relatively stable in the sodium dithionite system, but the degree of hydrolysis of the covalent bond in the sodium hydroxide solution can be enhanced by sodium dithionite. And the sodium dithionite can destroy the chromophore to achieve the purpose of decolorization.

Investigation Of The Decolorization On Cotton Substrate With Wide-angle X-ray Diffraction Analysis

In order to explore more information about the decolorization mechanism in the NaOH/$Na_2S_2O_4$ system, on both cotton fiber before decolorization and the decolorized cotton substrate samples at best craft were further investigated by utilizing wide-angle X-ray diffraction analysis. The achieved WAXRD patterns are depicted in Fig. 14.

Figure 14 shows that some variations in the X-ray diffraction patterns of the decolorization cotton samples were observed in comparison with the dyed control one, indicating some alterations of the crystalline structure of the cotton fibers occurred during decolorization. As shown in Fig. 14**(1)**, a typical WAXRD pattern of the reactive-dyed cotton fiber with a characteristic and dominant crystalline form of cellulose I was detected, accompanied with four broad peaks at the Bragg diffraction angles 2θ of 14.65°, 16.64°, 22.61°and 34.47°, respectively (French 2014; Zhu et al. 2017). Figure 14 the diffraction peak intensity of cotton fibers after decolorization decreased, respectively, in comparison with the dyed control sample, for all different dyed cotton fabric. These results indicate that only a small amount of the crystal zone of cotton fiber was damaged, and most of the crystal zone and crystal structure were not affected during the decolorization treatment. And Fig. 14 show that the separation of dyes was achieved during the decolorization treatment in the NaOH/$Na_2S_2O_4$ system since the dye was distributed in the amorphous phases area of the cotton fiber without affecting the chemical structure and crystalline structure of the cotton fiber, resulting in the loss of the strength loss of the cotton fabric after decolorization smaller. Importantly, these variations also disclose that the active species were able to diffuse into the inner phase of the cotton fiber to efficiently degrade the reactive dye molecules on the substrate chains, which further validates the mild mechanism for decolorization on Reactive-dyed cotton fabrics.

Conclusions

In this work, the decolorization properties and mechanism of cotton fabrics with different chromophores and active groups were investigated in the NaOH/$Na_2S_2O_4$ system in a targeted manner, especially. And the decolorization process and decolorization performance of reactive dyed cotton fabrics with different chromophores and active groups are also inconsistent. The achieved results disclose that NaOH hydrolyzes the covalent bond between dye and cotton fiber through hydrolysis reaction, and $Na_2S_2O_4$ destroys the chromophore through reduction reaction to achieve decolorization, and the proposed targeted decolorization method is very effective in removing reactive dye molecules from cotton fabric substrate, which can achieve mild decolorization and maintain a high retention rate of breaking strength. And the decolorization process and decolorization performance of reactive dyed cotton fabrics with different chromophores and active groups are also inconsistent. The dye on Reactive Red KE-3B dyed cotton fabrics is the most difficult to remove, and the dye on Reactive Red X-3B dyed cotton fabrics is the easiest to remove. Moreover, the mild decolorization mechanism of cotton substrate dyed with different chromophores and active groups was successfully characterized and investigated according to the alterations in chemical and aggregation structures, and surface morphologies of cotton fibers, by employing super depth of field microscope, Fourier transform infrared spectrometry (FT-IR) and wide-angle X-ray diffraction (WAXRD) analysis. All the investigations also indicate that the gentle decolorization of waste cotton fabrics can be achieved under the condition of normal pressure and high temperature in the NaOH/ $Na_2S_2O_4$ system without affecting the subsequent use of pulping.

Declarations

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Contributions

W. W and Y.Y have done the main job of this study.

W. W and Y.Y were responsible for investigation, data curation, and original draft. X.Z was responsible for review and editing. H. W, X.G, Z. G and P. Z were responsible for methodology and investigation. C.Z was responsible for conceptualization, methodology, supervision, and funding acquisition. All authors read, revised, and approved the final manuscript.

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Ethics declarations

Competing interests

The authors declare no competing interests.

Ethics approval

Not applicable.

Consent to participate

Not applicable.

Consent for publication

Not applicable.

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Figures

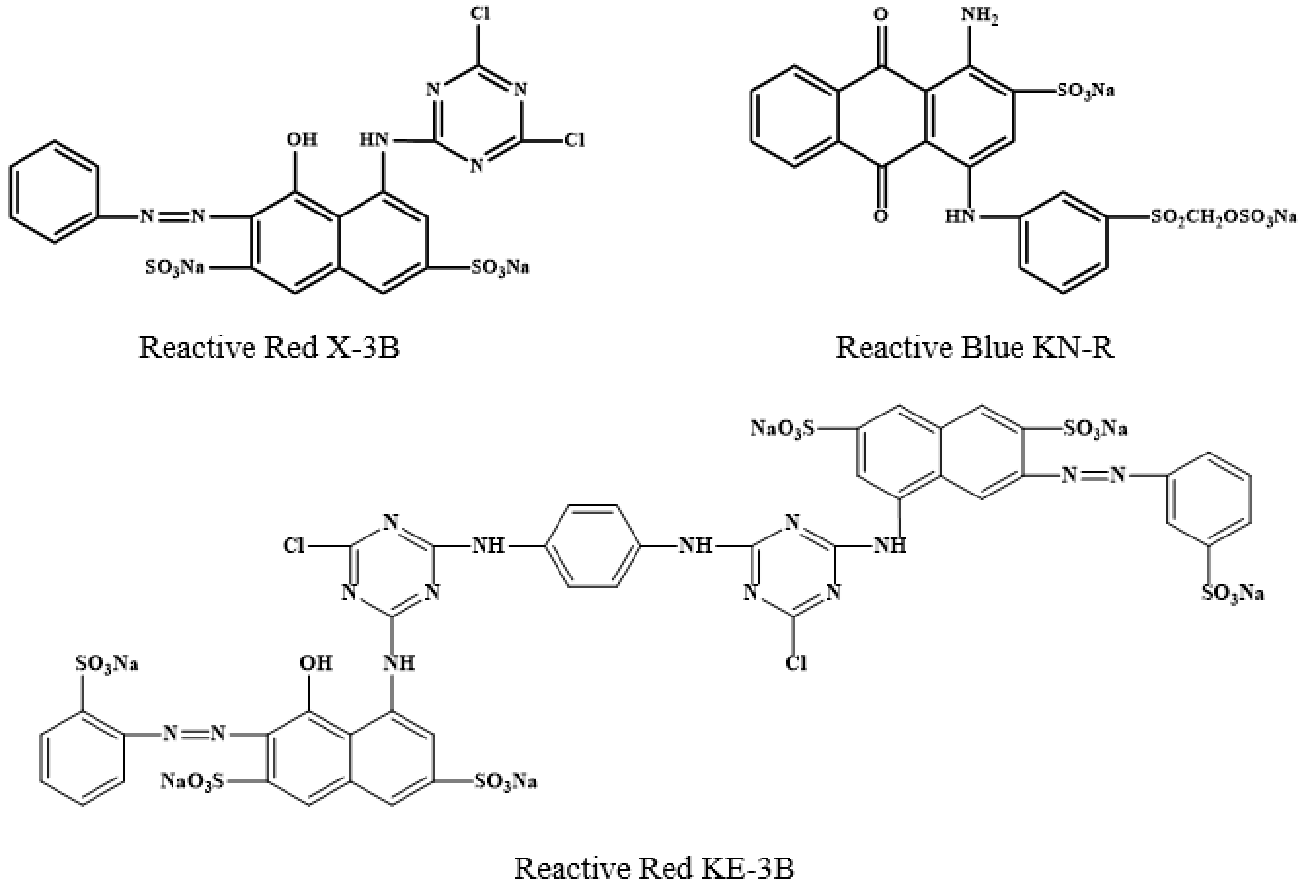

Figure 1

The chemical structure of the employed reactive dye

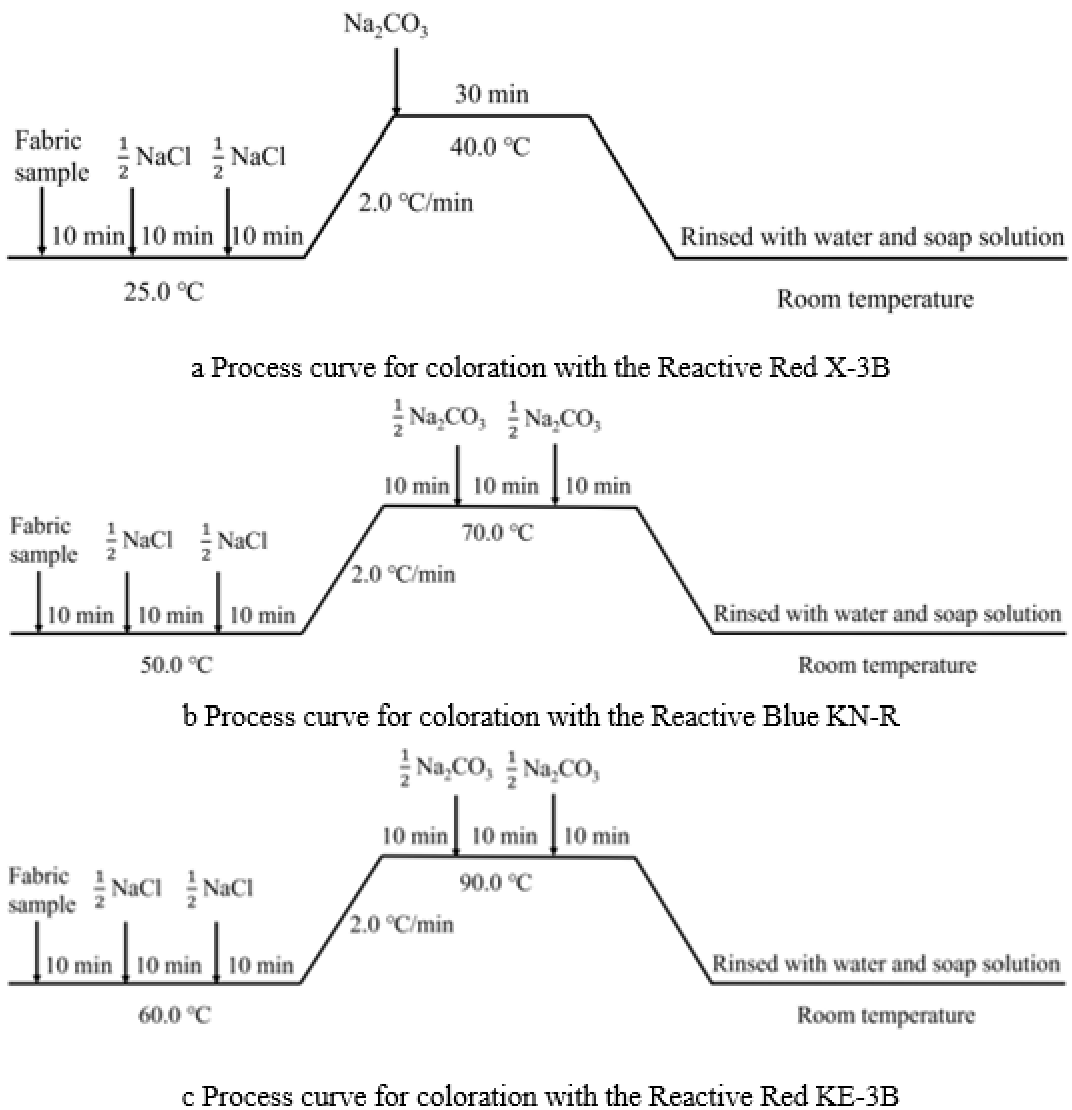

Figure 2

Parameter curve for cotton substrate coloration with the employed reactive dye

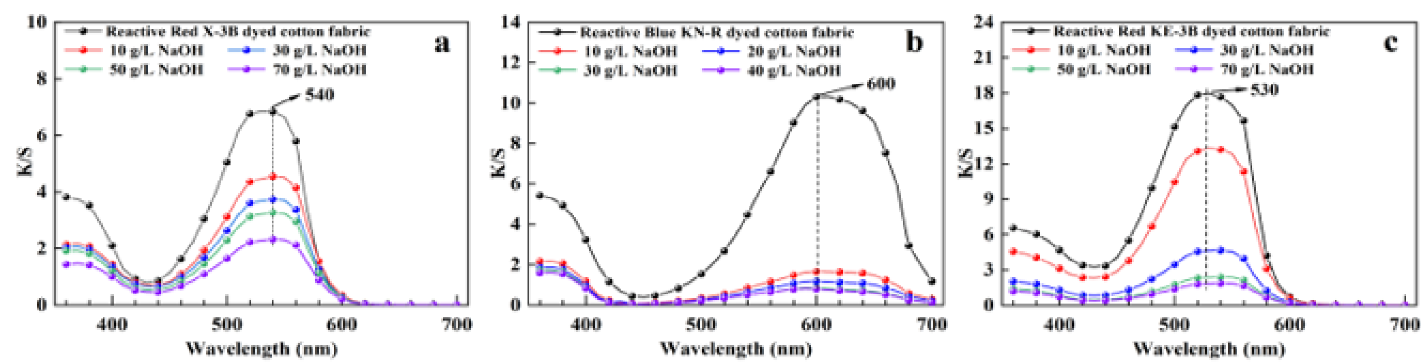

Figure 3

K/S value curves of different types of dyed-cotton fabrics decolorized by different concentrations of sodium hydroxide at the boiling temperature

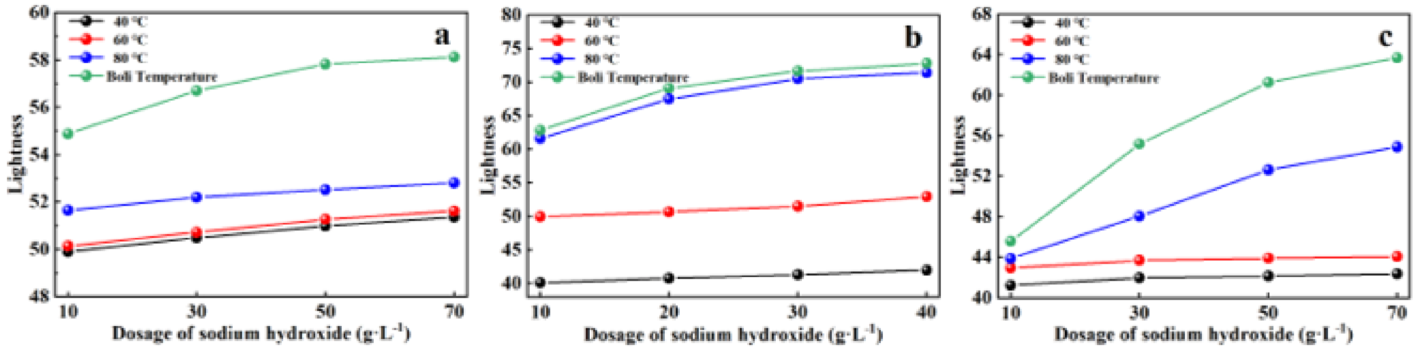

Figure 4

Lightness curves of (a) Reactive Red X-3B, (b) Reactive Blue KN-R, (c) Reactive Red KE-3B dyed-cotton fabrics decolorized by different concentrations of sodium hydroxide at a different temperature

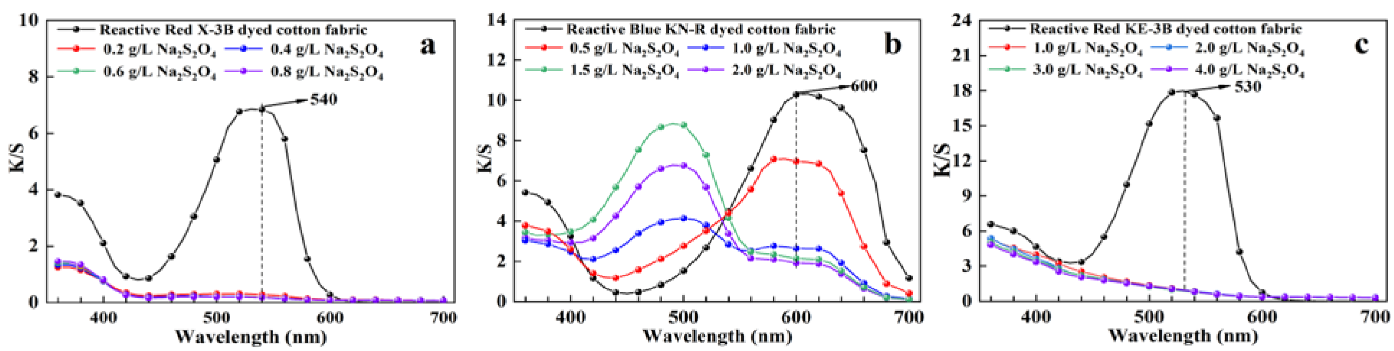

Figure 5

K/S curves of different types of dyed-cotton fabrics decolorized by different concentrations of sodium dithionite at the boiling temperature

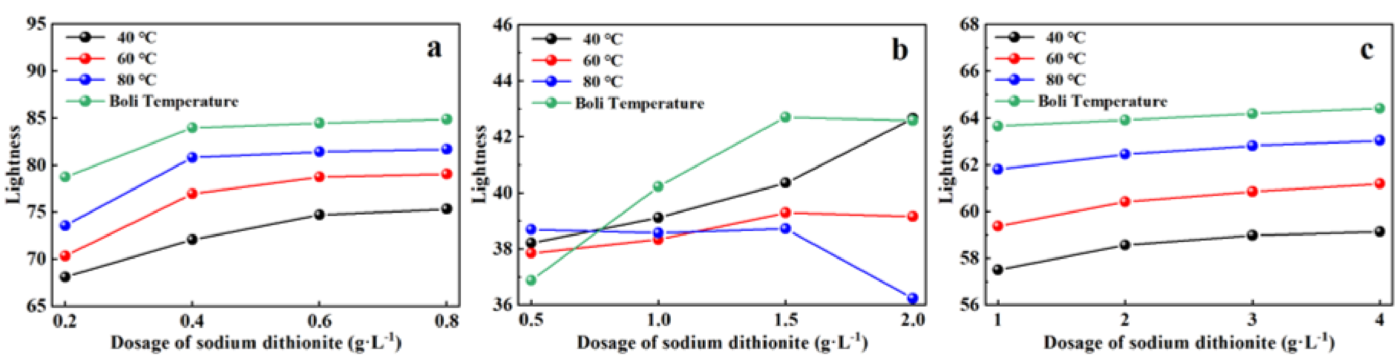

Figure 6

Lightness values of (a) Reactive Red X-3B, (b) Reactive Blue KN-R, (c) Reactive Red KE-3B dyed-cotton fabrics decolorized by different concentrations of sodium dithionite at a different temperature

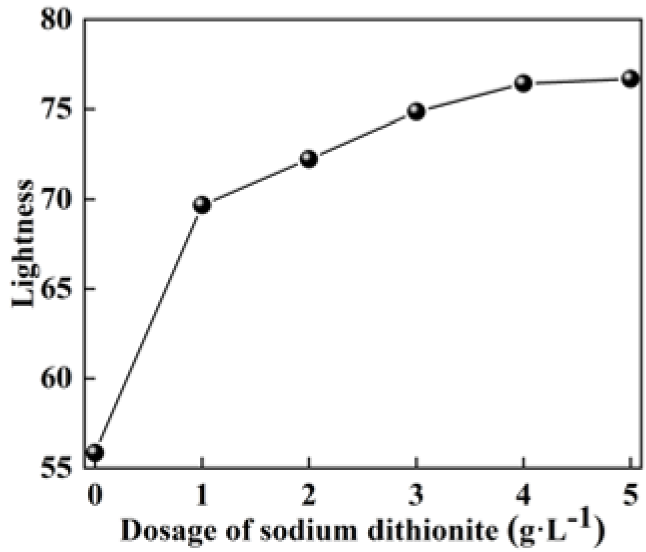

Figure 7

Influence of dosage of sodium dithionite on lightness values for dyed cotton fabrics

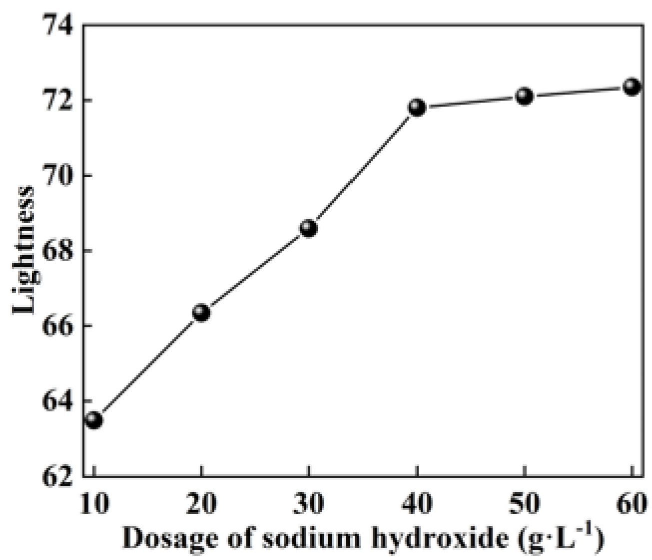

Figure 8

Influence of dosage of sodium hydroxide on lightness values for dyed cotton fabric

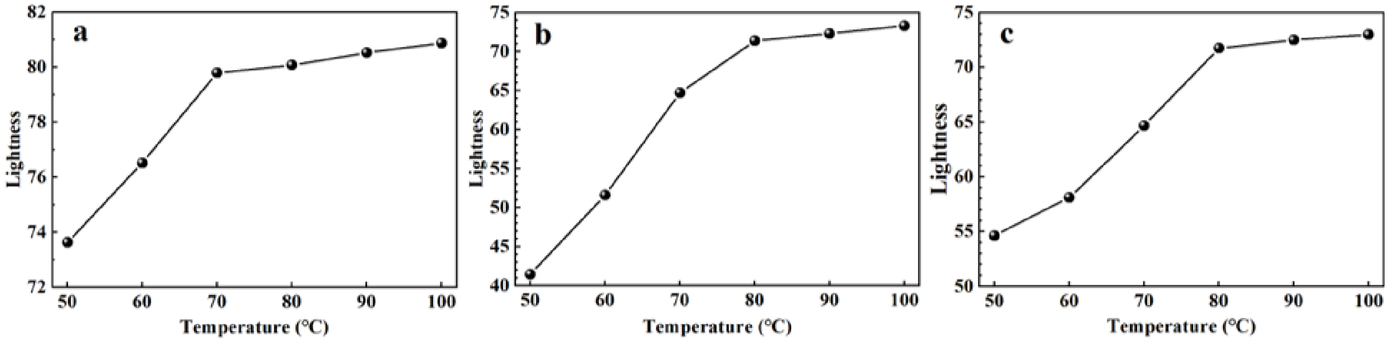

Figure 9

Influence of a different temperature on decolorization by different types of dyed-cotton fabrics

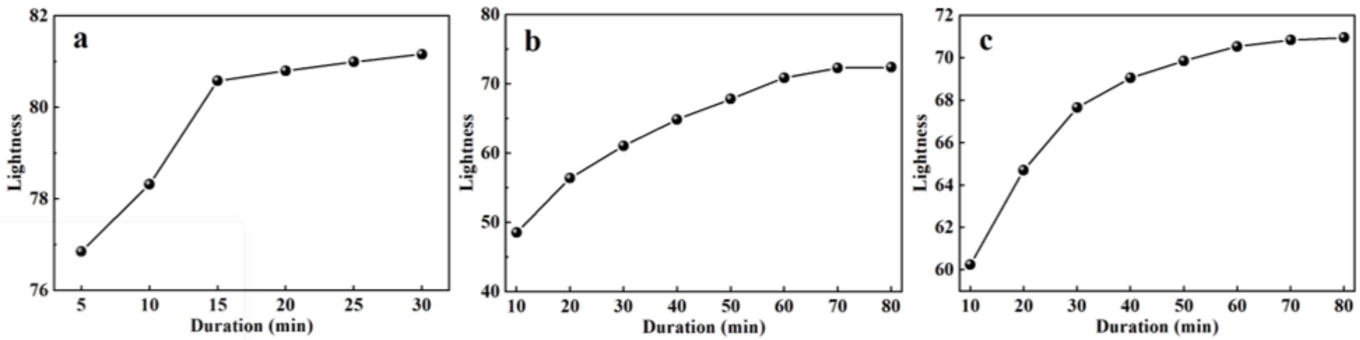

Figure 10

Influence of different durations on decolorization by different types of dyed-cotton fabrics

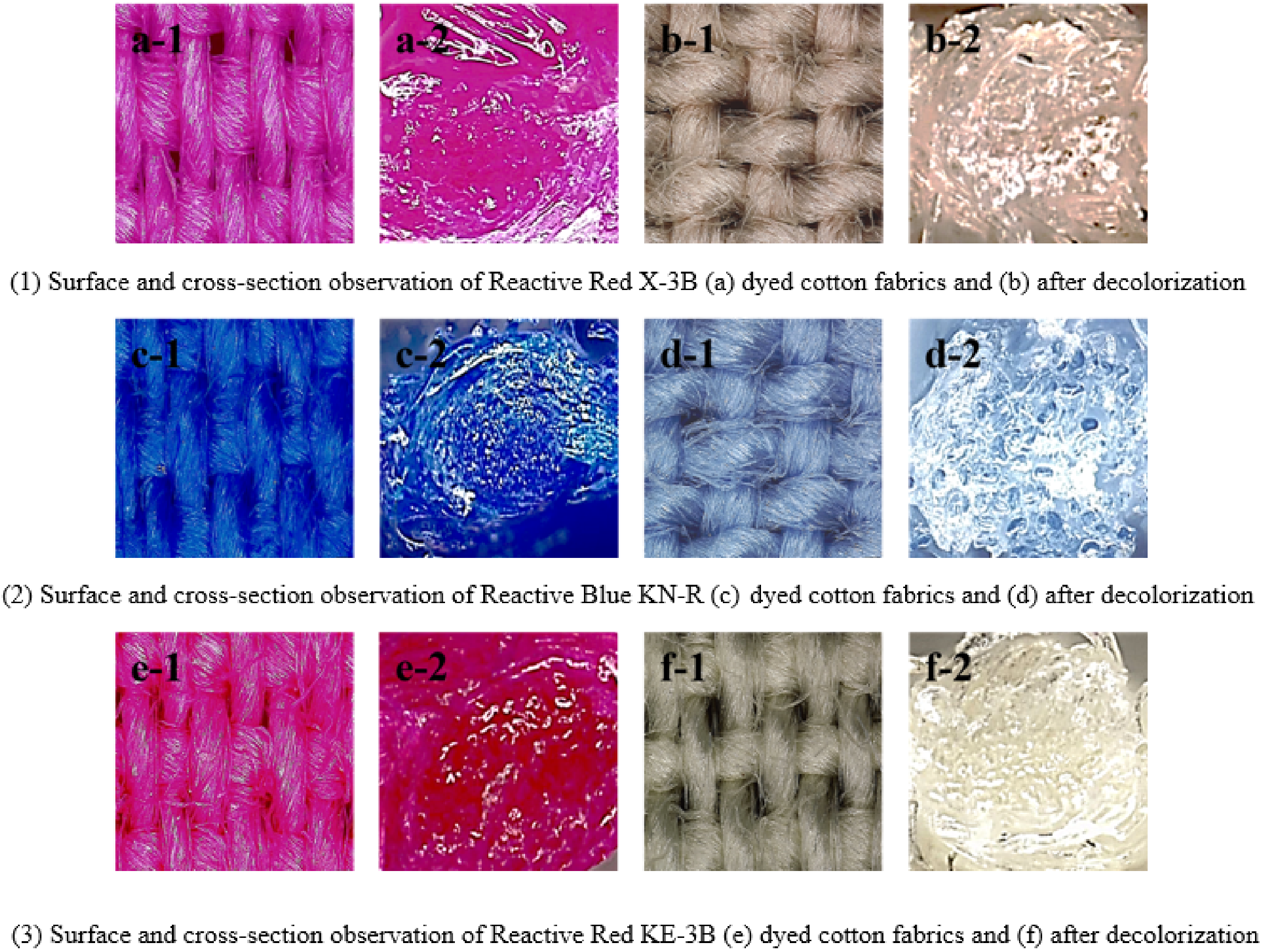

Figure 11

Surface observation about ×500 and cross-section observation of cotton fabrics before and after decolorization

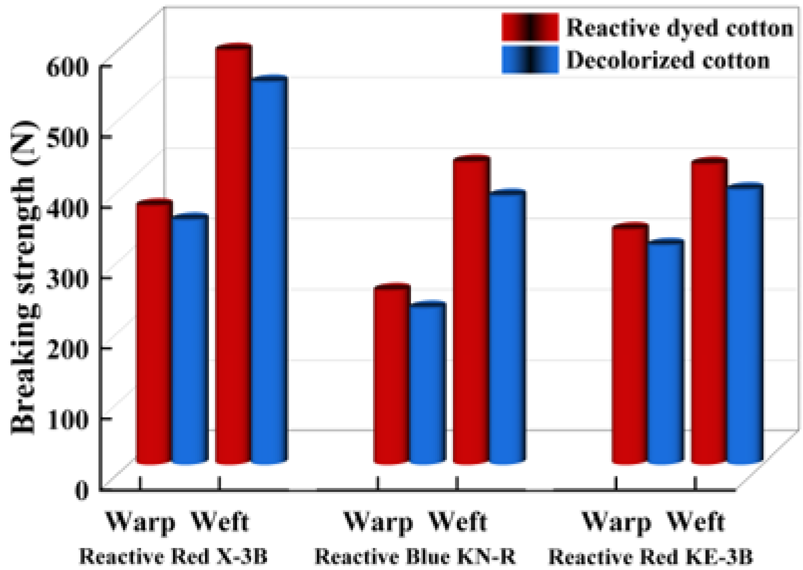

Figure 12

Breaking strength of cotton fabrics before and after decolorization

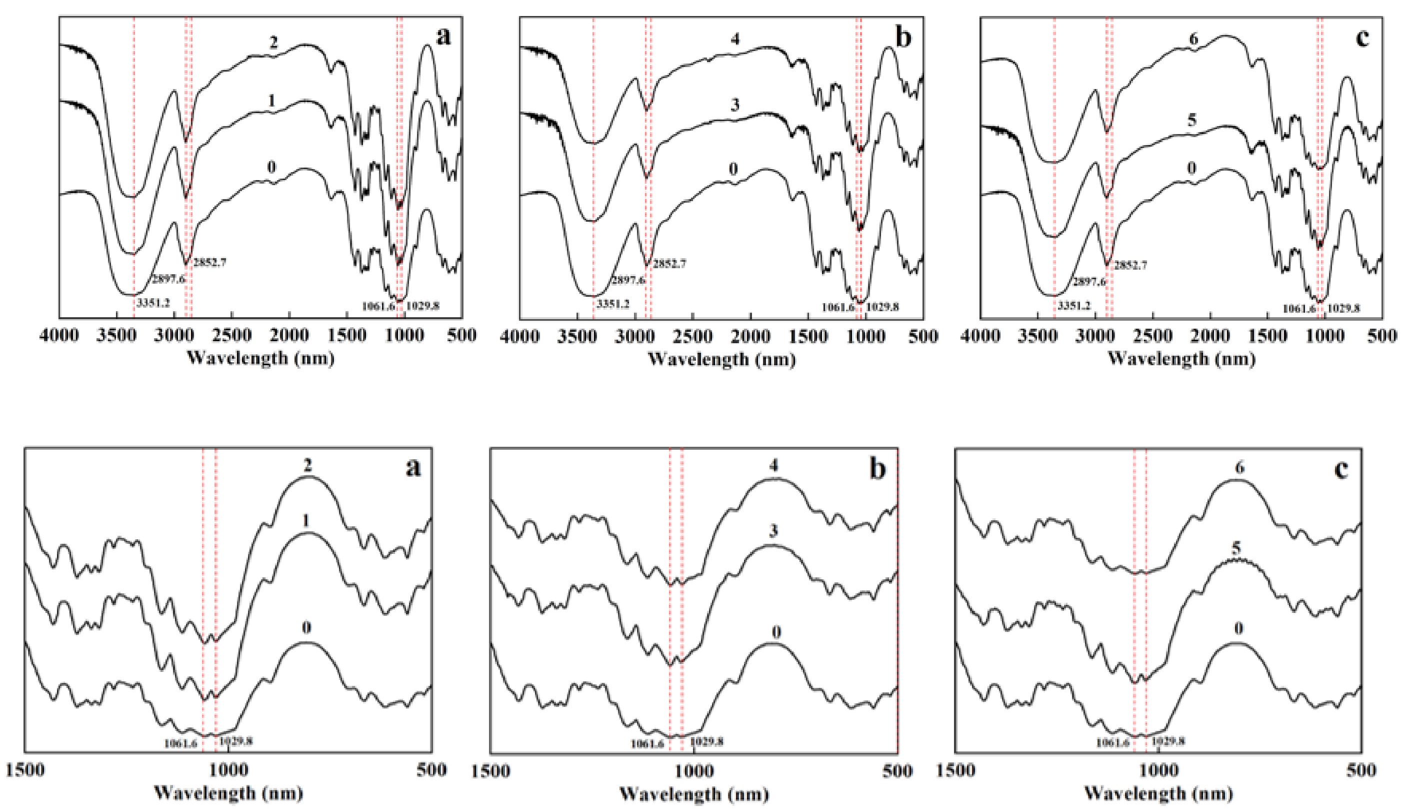

Figure 13

FT-IR spectra of cotton cellulose for (0) cotton fabric before dying, (1) Reactive Red X-3B dyed cotton fabric, (2) Reactive Red X-3B dyed cotton fabric after decolorization, (3) Reactive Blue KN-R dyed cotton fabric, (4) Reactive Blue KN-R dyed cotton fabric after decolorization, (5) Reactive Red KE-3B dyed cotton fabric, (6) Reactive Red KE -3B dyed cotton fabric after decolorization

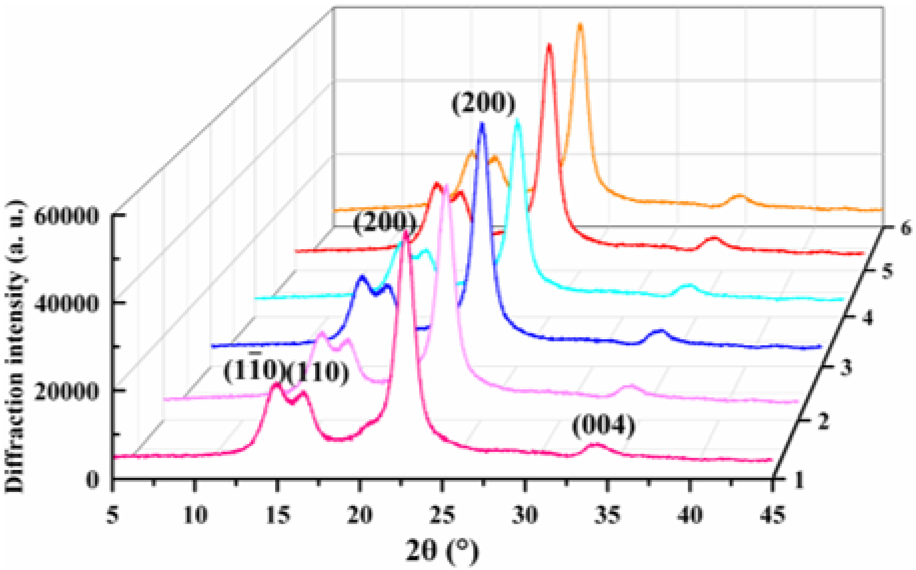

Figure 14

The WAXRD patterns of cotton samples for (1) Reactive Red X-3B dyed cotton fabric, (2) Reactive Red X-3B dyed cotton fabric after decolorization, (3) Reactive Blue KN-R dyed cotton fabric, (4) Reactive Blue KN-R dyed cotton fabric after decolorization, (5) Reactive Red KE-3B dyed cotton fabric, (6) Reactive Red KE -3B dyed cotton fabric after decolorization

Supplementary Files

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