The Adsorption Character of Kapok Fiber and Reactive Dyeing Technology on Modified Kapok Fiber

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ABSTRACT
The adsorption character of kapok fiber with direct dyes and the dyeing technology of cationic modified kapok fiber with reactive dyes were studied in this article. The results indicate that the optimal dyeing technique parameters for the cationic modified kapok fiber with the reactive dye Cibacron FN-R include 0.5~1% (o.w.f) of dyes, 15~20g·L^{-1} of NaCl, and 2g·L^{-1} of JFC with bath ratio of 1:50 at a dyeing temperature of 40℃ for 30min. The dyed kapok fiber was fixed with 15~20g·L^{-1} of Na_2CO_3 for 60min. As a result, the dye-uptake, fixation ratio, wash fastness, friction fastness, and K/S of cationic modified kapok fabric were enhanced by above technique.

Keywords: Kapok, Adsorption, Modification, Dyeing technology; Infrared spectrum.

INTRODUCTION

Kapok fiber is a natural and environmental-friendly cellulosic fiber with a lightweight of volume units, hollow structure, and no residue of pesticides and chemicals [1] [2]. Kapok fiber is also a heat and sound insulation material as well as a good filling and floating material [3] [4]. It is currently the only natural cellulosic fiber that has not been developed and applied in the field of dress adornments, due to its high stiffness, low cohesion, low spinnability, and low dye-uptake. Up to now, although the stiffness of kapok fiber had been effectively improved [5], dyeing performance of kapok fiber has not been systematically researched.

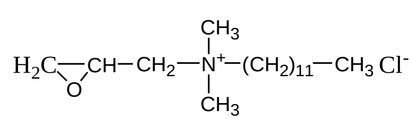
Previous research showed that kapok fiber can be dyed by direct dyes. However, due to the presence of a large amount of lignin and hemicellulose, the kapok fiber cannot be dyed. Thus, the dye-uptake of kapok is lower than other cellulosic fiber under the same conditions [6]. The difference is obvious. Moreover, there are a variety of dyes including direct dyes, reactive dyes, vat dyes, and azoic dyes having mature dyeing technologies that could be used for cellulosic fiber such as cotton and linen. Except for direct dyes, reports about other kinds of dyes applied on kapok fiber are rarely published. Also, direct dyes have nearly the lowest fastness compared to all the other known dyes, resulting in dyeing defects, such as uneven color and shades, difference in product fastness, and the presence of snowflake-shaped light-color defects, when blended and intertwined with other fibers. No solution has been studied worldwide. Also, some azo components in direct dyes cause damages to their user, and are internationally forbidden, greatly restricting the exportation and utilization of direct dyes.

Surface modification has been applied for some natural cellulosic fibers, such as cotton and linen [7] [8] [9]. But the modification of kapok fiber has not been reported.

Aspiring to change the current single dye for kapok fiber, the method of dyeing kapok fiber with reactive dyes was studied in this article, and also cationic modification was applied to improve dyeing properties of reactive dyes. In order to provide the basic experimental data for the theoretical study on the dyeing performance of kapok fiber, the adsorption character of kapok fiber with direct dye Solophenyl red 3BL was also studied.

EXPERIMENTAL MATERIALS

The kapok fiber was provided by Shanghai Textile Holding (Group) Corporation (Shanghai, China). The cationic modification agent structure shown below with 40% solid content synthesised us.



Direct dye Solophenyl red 3BL and reactive dye Cibacron FN-R were provided by Hunsman Inc (Shanghai, China). Other PC or AR chemical agents were purchased from the chemical market.

EXPERIMENTAL METHOD

The Modification of Kapok Fiber

After being scoured and bleached, the kapok fibers were treated with 8% (o.w.f) of the modification agent with a pH value of 11, treatment temperature of 75℃, and treatment time of 45 min, and then washed to be neutral and dried.

The Method of Dyeing

The dye bath was composed of dyes, penetrating agent fatty alcohol polyoxyethylene ether (JFC), and NaCl. The modified kapok fiber was put into the dye bath for 30min, and was fixed with Na_2CO_3 for 60min. The dye process curve of reactive dyes is shown in *Figure 1*.

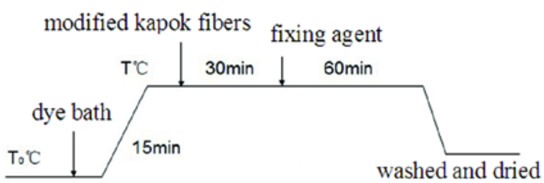


FIGURE 1. The dye process curve of reactive dyes.

The Morphological Characterization of Fiber

A scanning electron microscope (SEM, JSM-5600LV from Japan) was used to characterize the fiber surface morphology by spreading gold on the fibers in vacuum. The test condition was acceleration voltage-5KV and current-5mA.

The Infrared Spectra Test

The chemical structure of modified kapok fiber was analyzed by Fourier transform infrared spectroscopy (FT-IR) spectra recorded on a Nicolet IR2000 spectrophotometer in the transmission mode.

The Dye-uptake Test

The dye-uptake was tested by the method of remaining dye concentration in the dye bath at the maximum absorption wavelength λ_{max}=611nm, and then calculated by the reduction formula Eq. (1) as follows [10]:

$$\text{Dye-uptake}\ (\%) = \left[1 - \left(\frac{C}{C_0}\right)\right] \times 100\% \qquad (1)$$

where C_0 is the initial dyes' concentration in the dye bath, and C is the remaining dyes' concentration in the dye bath.

The Fixation Ratio Test

The dyed fiber was washed by water for 5min and soaped for 15min with 2g·L^{-1} of standard soap at 90 ℃ and washed again with water. The optical density of the mixed liquid involving the remaining dye bath and the washing liquid as well as soaping liquid and the initial standard dye bath was tested by spectrophotometer. The fixation ratio was calculated by the reduction formula Eq. (2) as follows [10]:

$$\text{Fixation ratio}\ (\%) = \left[1 - \left(\frac{nA_1}{mA_0}\right)\right] \times 100\% \qquad (2)$$

where m and n are the diluted multiple of initial dye bath and mixed liquid, A_0 and A_1 are the optical density of the initial the dye bath and the mixed liquid.

The K/S Test

The K/S was tested at 5 points at the wavelength λ_{max} =611nm on Color Quest XE made by Hunter Lab Inc, then the average value was calculated.

The Fastness Test

The wash fastness was tested on the basis of Chinese standard GB / T3921(1)-1997.

The friction fastness was tested on the basis of Chinese standard GB / T3920-1997.

RESULTS AND DISCUSSION

The Adsorption Character of Kapok Fiber with Direct Dye

The kapok fiber was dyed with Solophenyl red 3BL at the concentrations of 3, 4, 5, 6, 7 and 8% (o.w.f) for 3h at 70℃ with bath ratio of 1:50, the dye-uptake calculated by Eq.(1) was 33, 38, 42, 45 ,45 and 47%.

The concentration of dye on the fiber ($[D]_f$) and the dye bath ($[D]_s$) were then calculated. The relation between the lg$[D]_f$ and the lg$[D]_s$ is shown in *Figure 2*.

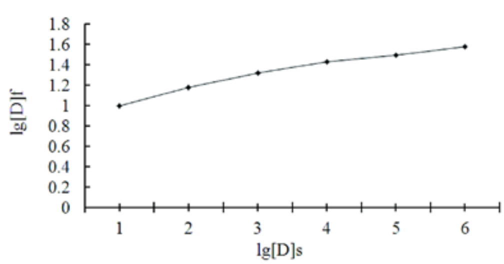


FIGURE 2. The relation between the lg$[D]_f$ and the lg$[D]_s$, $[D]_f$ was the concentration of dye on the fiber and $[D]_s$ was the concentration of dye in the dye bath.

The relation between the $\lg[D]_f$ and the $\lg[D]_s$ (shown in *Figure 2*) can regarded as a linear relation. The linear equation was expressed as Eq. (3) through linear regression:

$$\lg[D]_f = 1.80 + 0.79\lg[D]_s \tag{3}$$

The empirical equation of the adsorption isotherm of the direct dyes Solophenyl red 3BL on kapok fiber was expressed as Eq. (4):

$$[D]_f = 63[D]_s^{0.79} \tag{4}$$

The dyeing adsorption isotherm of direct dye Solophenyl red 3BL on kapok fiber was a type of Freundlich adsorption isotherm according to Eq. (4). The adsorption of the direct dye Solophenyl red 3BL on kapok fiber was a type of physical adsorption. The concentration of dyes on kapok fiber increased with the increment of the concentration of dye in the dye bath, and the increase rate decreased slowly, because the dye was adsorbed on the surface of fiber, and dye molecule was distributed evenly in the dye bath due to molecular thermal motion of dye. Thus a diffusion adsorption layer would form on the interface. As for the diffusion adsorption layer, the dye concentration decreased gradually until it was similar to that of the dye bath.

The Dye-uptake of Reactive Dye of Scoured Kapok Fiber

The scoured kapok fiber was dyed by 1% (o.w.f) of the reactive dye Cibacron FN-R for 100 min with bath ratio of 1:50 at temperatures of 40, 50, 60 70 and 80℃. The relation between the dye-uptake and the dye temperature is shown in *Figure 3*.

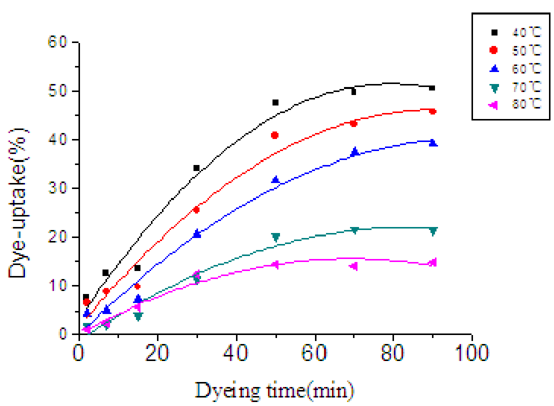


FIGURE 3. The relation between the dye-uptake on scoured kapok fiber and the different dye temperature.

As shown in *Figure 3*, the dye-uptake of scoured kapok fiber decreased with the increase of temperature. The dye-uptake was about 50% at 40℃ while it decreased sharply to 10-15% when the temperature increased to 70-80℃. When the dyeing temperature increased, although the adsorption rate increased, the resolution rate also increased, hence the dye-uptake decreased on the contrary.

The Influence of Alkali Treatment on Dye-uptake and Morphology of Kapok Fiber

Because there is a large amount of lignin and hemicellulose in kapok fiber, the alkali treatment was studied in this paper in order to improve the dye-uptake. Kapok fiber was treated by NaOH solution without tension for three minutes. The influence of alkali liquor density on dye-uptake is shown in *Table I*.

TABLE I. The influence of alkali liquor density on dye-uptake.

Density of alkali liquor （g·L-1）	0	120	150	180	210	240	270
Dye-uptake （%）	53	67	71	72	72	73	72

As shown in *Table I*, the dye-uptake of kapok fiber was raised from 53% to 73% after the alkali treatment. The dye-uptake rate increased with the increase of alkali solution density and became constant until the density was or up to 180g·L^{-1}.

Although the dye-uptake of reactive dye on kapok fiber increased by alkali treatment, the hollow structure of kapok fiber was destroyed, indicating that the kapok fiber lost its warm-keeping property. Thus, alkali process may not be a suitable method for the dye-uptake increase of reactive dye on kapok fiber.

Due to the obvious defects of alkali treatment, the cationic modification used to increase the dye-uptake of reactive dye on kapok fiber was studied in this article.

The Characterization of Cationic Modified Kapok Fiber by Infrared Spectroscopy (FT-IR)

The scoured and bleached kapok fiber was modified by 8% (o.w.f) of modification agent at the temperature of 75℃ for 45 min, and then was measured by Fourier transform infrared spectroscopy (FT-IR) spectra as seen in (*Figure 4*).

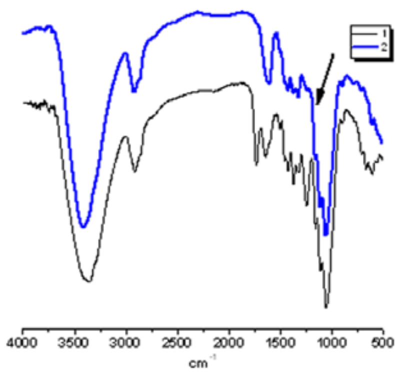


FIGURE 4. The infrared spectra of unmodified and modified kapok fiber, line 1 was unmodified kapok fiber, line 2 was modified kapok fiber.

As shown in *Figure 4*, the adsorption peaks of modified kapok fiber in the 1510~1245cm^{-1} region (marked with arrow in *Figure 4*) decreased or vanished. The character peaks in this region were generally regarded as the stretch tensor of C-O(C-O st) and the surface bending or shear vibration of O-H (O-H δ) [11]. The reason for the change of the adsorption peak could be that the surface bending or shear vibration of O-H (O-H δ) was restricted because of the long chain of aliphatic hydrocarbons $-(CH_2)_{11}-CH_3$ grafted on the modified kapok fiber.

The strong characteristic adsorption peak of amine was in the 3500~3300cm^{-1} region. Also, the characteristic adsorption peaks of the stretch tensor of O-H (O-H st) and the stretch tensor of C-H (C-H st) were also in this region. So there was no practical value to characterize the effect of cationic modification using the adsorption peak in 3500~3300cm^{-1}.

The structure of kapok fiber was hardly changed after cationic modification treatment (as shown in *Figure 5 and Figure 6*).

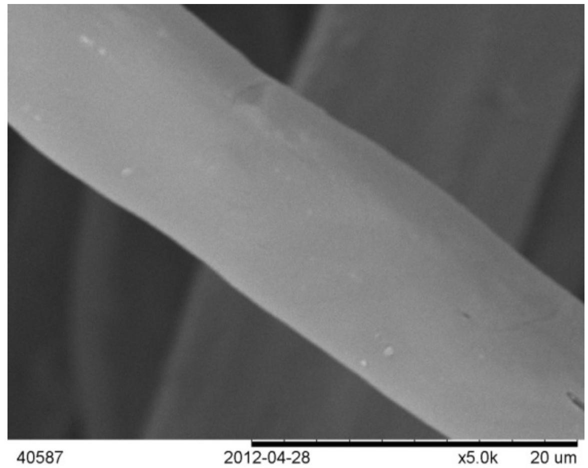


FIGURE 5. The morphology of scoured kapok fiber.

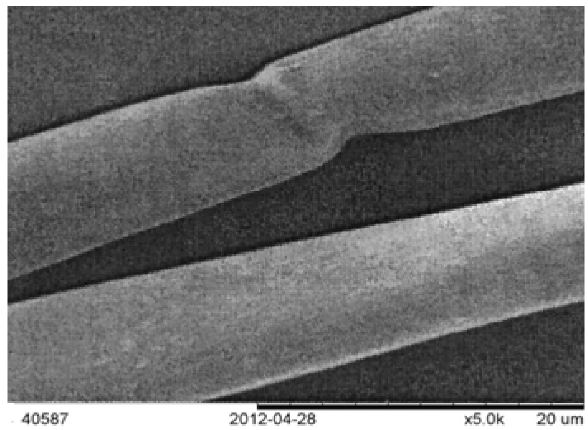


FIGURE 6. The morphology of cationic modified kapok fiber.

<u>The Influence of Reactive Dyes Concentration on the Dye-uptake</u>

The modified kapok fiber was dyed respectively by the reactive dye Cibacron FN-R at the concentration of 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5, 3.0 and 4.0% (o.w.f) for 30min with 20$g\cdot L^{-1}$ of NaCl and 2$g\cdot L^{-1}$ of JFC at the temperature of 60℃ at bath ratio of 1:50, and then the dyed kapok fiber was fixed for 60 min by 15$g\cdot L^{-1}$ of Na_2CO_3. The relation between the dye-uptake and the concentration of reactive dyes is shown in *Figure 7*.

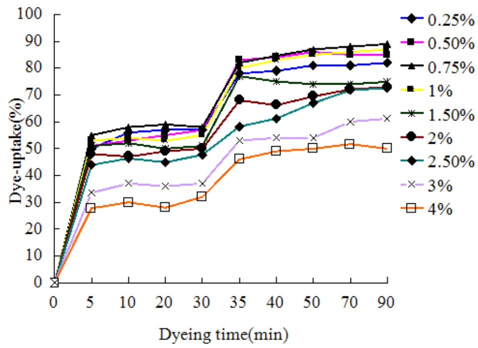


FIGURE 7. The relation between the dye-uptake on modified kapok fiber and the different concentration of reactive dye.

In the dye bath, the kapok fiber was electronegative due to the ionization of cellulose fiber, and the reactive dye was anionic. Modification treatment could reduce or remove negative charge on fiber. So the adsorption ability of kapok fiber could be enhanced. Meanwhile, the dye-uptake of reactive dyes could be enhanced by increasing the dye site of reactive dyes in the fiber.

The high dye-uptake could be obtained while the reactive dyes concentration ranged 0.5% to 1% (o.w.f). When the dye concentration was over 1%, the dye-uptake would decrease to varying degrees not only in the process of dyeing but also in the process of fixation. The dye was present in the dye bath in the form of the molecule, micelle, aggregate, and solid. Generally, the dye in the form of the molecule and a small micelle could be adsorbed by fiber. The dye-uptake would be low at the high concentration of dyestuff because the quantity of dyestuff in the form of the aggregate increased and solid dyestuff and dyestuff micelle would adsorb a part of dyestuff molecule [12]. The reactive dye concentration was chose in the range of 0.5~1% (o.w.f).

The Influence of Dye Temperature on the Dye-uptake

The modified kapok fiber was dyed by 1% (o.w.f) of the reactive dye Cibacron FN-R for 30min with 20g·L^{-1} of NaCl and 2g·L^{-1} of JFC at bath ratio of 1:50 at the temperature of 30, 40, 50, 60 and 70℃ respectively, and then the dyed kapok fiber was fixed with 15g·L^{-1} of Na_2CO_3 for 60 min. The relation between the dye-uptake and the dye temperature is shown in *Figure 8*.

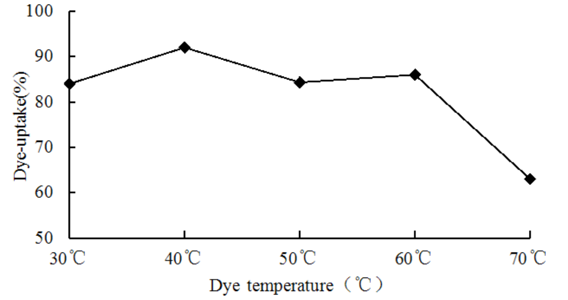
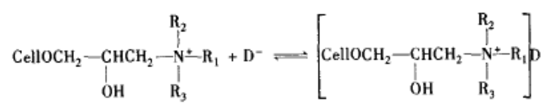


FIGURE 8. The relation between the dye-uptake on modified kapok fiber and the different dye temperature.

The cationic modification agent was quaternary ammonium with C_{12} aliphatic hydrocarbons which could be cross linked with the hydroxyl on the kapok fiber. Thus the modified kapok fiber surface had some positive charges so as to adsorb reactive dyes by electron-positron attractions. The dye-uptake of reactive dye on kapok fiber could be enhanced. The adsorption of reactive dye on modified kapok fiber could be expressed as follows:



Meanwhile, reactive dye could be adsorbed on kapok fiber by substantively due to the macromolecular structure of cellulose. Two ways of reactive dye adsorption on modified kapok fiber could be considered. The one was the Coulomb force attracting between the anionic dye and modified kapok fiber with electron-positron partly on its surface. The other was dependent on the substantively between the reactive dyes and cellulose fiber. The dye temperature is an important factor in the dyeing of reactive dye. At high temperature, the adsorption rate and desorption rate would both increase, resulting in the decrease of balance ratio of dye-uptake. The dye-uptake of reactive dyes on a modified kapok fiber reached the highest at the temperature of 40 ℃ and the lowest at the temperature of 70℃.

The Influence of NaCl Amount on Dye-uptake

The phenomenon of the high strike and the unlevel dyeing would emerge because of the uneven distribution of cationic modification agent on the kapok fiber. As for the modified kapok fiber dyed by reactive dye, on one hand NaCl was used as the retardant for dye which was adsorbed by kapok fiber by the attraction of Coulomb force. On the other hand NaCl was used as the accelerant for dye which was adsorbed by kapok fiber by the substantively between the dye and kapok fiber. So, the NaCl amount was one of the key factors affecting dye-uptake.

The modified kapok fiber was dyed by 1% (o.w.f) of the reactive dye Cibacron FN-R for 30 min with 0, 5, 10, 20, 30 and 40g·L^{-1} of NaCl respectively and 2g·L^{-1} of JFC at bath ratio of 1:50 at temperature of 40℃, and then the dyed kapok fiber was fixed for 60 min with 15g·L^{-1} of Na_2CO_3. The relation between the dye-uptake and dose of NaCl was shown in *Figure 9*.

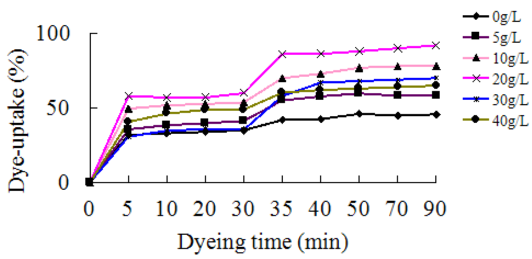
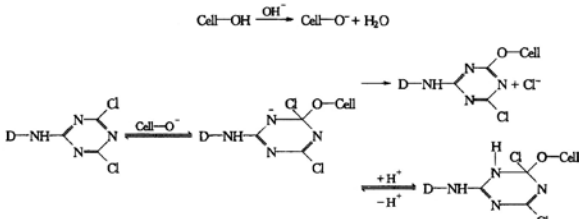


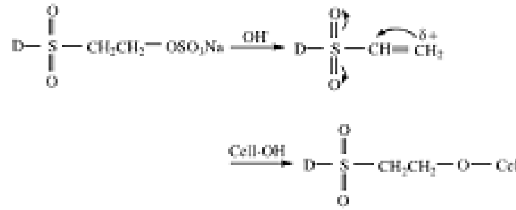
FIGURE 9. The relation between the dye-uptake on modified kapok fiber and the NaCl amount.

The dye-uptake of the reactive dye on modified kapok fiber was enhanced with increase of NaCl amount. When the NaCl amount was too high, the dye-uptake decreased. This phenomenon was due to the aggregate of the dye in the dye bath as NaCl concentration was high. The suitable NaCl amount was chosen as 15~20g·L^{-1} in this article as shown in *Figure 9*.

The Influence of the Fixing Agents Na_2CO_3 Amount on Dye-uptake

There are bifunctional groups such as triazine and vinyl sulfone in the structure of reactive dye Cibacron FN-R. The crosslinking reaction between the fiber and dye under alkaline conditions can be expressed as follows:





So, the amount of fixing agents Na_2CO_3 was also one of the key factors affecting dye-uptake.

The modified kapok fiber was dyed by 1% (o.w.f) of the reactive dye Cibacron FN-R for 30 min with 20g·L^{-1} of NaCl and 2g·L^{-1} of JFC at bath ratio of 1:50 at temperature of 40℃, and then the dyed kapok fiber was fixed for 60 min with 5, 10, 15, 20, 25, 30, 35 and 40g·L^{-1} of Na_2CO_3 respectively. The relation between the dye-uptake and the use of Na_2CO_3 was shown in *Figure 10*.

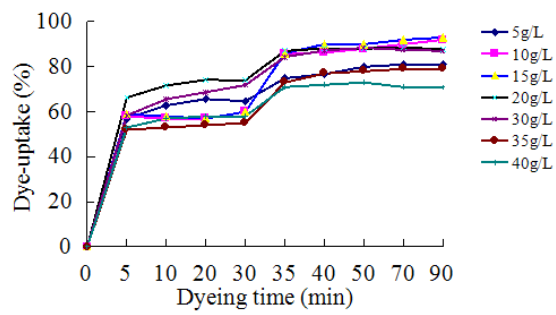


FIGURE 10. The relation between the dye-uptake on modified kapok fiber and the different concentration of fixing agent.

The fixation reaction between the active dye and cellulosic fiber occurred in the present of alkali. The crosslinking between the fiber and dye which adsorbed on fiber caused the reduction of the dye content on the fiber, and the adsorption balance was broken. The dye in the dye bath could further adsorb on the fiber and the dye uptake ratio could be enhanced. The fixation reaction between reactive dye and fiber was related with content of fixing agent. Less fixing agent led to the insufficient ionization of cellulosic fiber, resulting in the reduction of cross-linking between the dye and fiber. However, two more fixation agents led to the hydrolysis of dye. The hydrolyzed dye lost reactivity and could not cross link with fiber. In this article, the dye-uptake of the reactive dye Cibacron FN-R on modified kapok fiber was over 90% with the 15~20g·L^{-1} of Na_2CO_3 as shown in *Figure 9*.

The Dye Effect of Kapok Fabric with Reactive Dye Cibacron FN-R

The modified and the unmodified kapok fabrics were dyed by 1% (o.w.f) of the reactive dye Cibacron FN-R for 30 min with 20g·L^{-1} of NaCl and 2g·L^{-1} of JFC at the bath ratio of 1:50 at a temperature of 40℃, and then fixed for 60min with 20g·L^{-1} of Na_2CO_3. The dye-uptake, fixation ratio, wash fastness, friction fastness and K/S of modified and unmodified kapok fabric are shown in *Table II*.

TABLE II. The contrast of dyeing properties (include dye-uptake, fix-ratio, washing-fastness, friction-fastness and K/S) of unmodified kapok fabric (A) and modified kapok fabric (B).

	Dye-uptake (%)	Fix-ratio (%)	Washing-fastness (grade)	Friction-fastness (grade)		K/S
				Dry	Moisture	
A	53	24	4	3~4	3~4	2.8
B	94	65	4~5	4	4	7.5

Compared with unmodified kapok fabric, the dye uptake ratio of modified kapok fabric was raised by approximately 80% (rising from 53% to 94%), fixation ratio was raised by 170% (rising from 24% to 65%), washing-fastness was raised by half grade (rising from 4 grade to 4-5 grade), dry friction fastness was raised by half grade (rising from 3-4 grade to 4 grade), moisture friction fastness was raised by half grade (rising from 3-4 grade to 4 grade) and K/S value was raised from 2.8 to 7.5.

CONCLUSION

The adsorption of direct dye Solophenyl red 3BL on kapok fiber was mainly physical adsorption. The adsorption isotherm was similar to the Freundlich adsorption isotherm. The dyeing conditions for the modified kapok fiber dyed by active dye Cibacron FN-R included 0.5~1% (o.w.f)of dye, 15~20g·L^{-1} of NaCl and 2g·$L^{-1}$of JFC at the bath ratio of 1:50 at dyeing temperature of 40℃ for 30 min, and then the dyed kapok fiber was fixed for 60 min with 15~20g·L^{-1} of Na_2CO_3. Compared with unmodified kapok fabric, the dye uptake ratio, fixation ratio, wash fitness, friction fitness, and K/S value of modified kapok fabric showed a good improvement.

ACKNOWLEDGMENTS

This research was funded by a grant from the Shanghai Textile Holding (Group) Corporation Science Foundation (D-6000-08-4071-(08)) and the Science Foundation of Shanghai University of Engineering Science (A-2500-08-01003-2008XZ03). The authors wish to thank Dr. Bi Xu of College of Chemistry, Chemical Engineering and Biotechnology, Dong Hua University for his help and efforts in completing this research.

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