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Application of Complex Green Reducing Agents in Indigo Dyeing

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Abstract: Indigo is one of the most important vat dyes in the textile industry, and it must be reduced to a water-soluble leuco form before dyeing. This study aims to seek a complex green reducing agent as a possible substitute for the environmentally unfavorable sodium dithionite (SD) used in indigo dyeing. Firstly, the stability of three reducing agents, SD, thiourea dioxide (TD) and glucose (GS), is compared. The reduction system of indigo dyeing with TD can maintain good stability after 2 h vigorous stirring. However, SD and GS cannot reach the reduction potential required by indigo after 1 h vigorous stirring, and the dyeing performance of indigo decreased. Considering that GS is more eco-friendly than SD, the complex of TD and GS is selected as the green reducing agent of indigo dyeing. Secondly, the reduction potential, pH and *K/S* values for indigo dyeing on cotton fabrics with different mass ratios of the complex reducing agents are analyzed. The results show that the optimum mass ratio of TD to GS is 7∶3, and under this condition, a stable reduction potential and a high dyeing ability are obtained.

Key words: indigo dyeing; thiourea dioxide (TD); glucose (GS); sodium dithionite (SD); reduction potential; *K/S* value

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0 Introduction

Indigo is one of the most important vat dyes in the textile industry, and it has a distinctive blue color. It is used extensively for dyeing cotton yarns in the manufacture of denim and is practically insoluble in water with no substantivity for cellulosic fibers[1-2]. To enable cellulosic dyeing, indigo is reduced to its leuco soluble form (with yellow and green) which has substantivity for cellulosic fibers through van der Waals forces[3-4]. The reduction-oxidation reaction of indigo is shown in Fig. 1. Under the action of the reducing agent, the indigo dye begins to change into a non-ionic hydroxyl compound, which is called leuco acid. If sufficient reducing and alkali agents are present, the leuco acid could be reduced to water-soluble monophenol sodium ionic form. The mono-ionic form of leuco indigo is predominant in solution with the pH value around 11.5 and indigo in the mono-ionic form exhibits a high affinity to cellulosic fibers. When natural textiles such as cotton or linen are impregnated in this dye bath, the leuco indigo is adsorbed on cellulosic fibers, then the leuco indigo will be oxidized by air and turns back to the water-insoluble indigo, resulting in a blue shade on the fiber. The di-anion form of leuco indigo is present when the reducing and alkali agents are greatly excessive, and the solubility is greatly improved which exhibits a much lower affinity to cellulose, resulting in dyeing lighter[5-6].

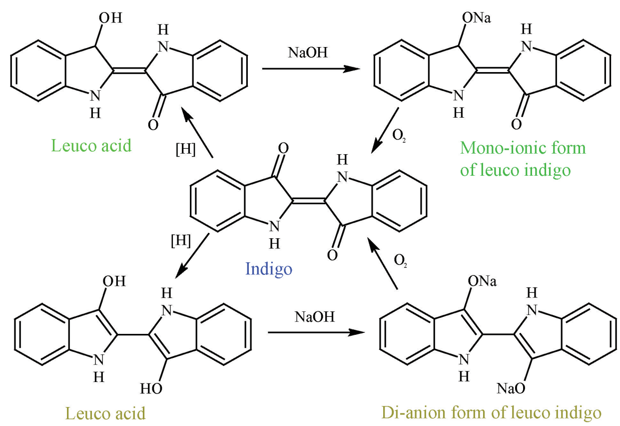

Fig. 1 Reduction-oxidation reaction of indigo

The reduction process of indigo is the key link of dyeing. Various reducing agents and techniques have been employed for indigo dyeing. The traditional reducing agents for industrial indigo dyeing are inorganic reductants, such as sodium dithionite (SD) and thiourea dioxide (TD). Due to the powerful reducing ability of SD, at present, reduction dyeing is mainly carried out by the traditional indigo reduction method which uses SD as a reductant in the factory[2]. However, the ecological drawbacks of SD are gradually being awared, such as low stability, corrosive effect, risks of fire and health

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problems during its storage, and generation of non-regenerable oxidation products like sulfite and sulfate which cause various problems to the disposal waste waters[7]. For a long period, many attempts have been made to design eco-friendly routes for indigo dyeing such as electrochemical techniques[8-9], inorganic Fe(II) ion-reducing agents and fermentation by bacteria, but none of them have been adapted to large-scale dyeing. The advantage of electrochemistry for indigo reduction is that it minimises the utilization of chemicals and makes the indigo dyeing process clean. However, a large consumption of electrical energy and the requirement of electrodes with high surface area need to be considered[5].

The first indigo dyeing procedures used in ancient times were fermented or bacterial indigo dye baths. For bacteria induced reduction, Aino et al.[10] found that strains belonging to the genera *Amphibacillus* and *Oceanobacillus* had major roles in supporting the reduced state of indigo during fermentation. Shin et al.[11] used *Saccharomyces cerevisiae strains* from baker's yeast powder and Korean rice wine, respectively, as alternative chemical reductants. Nevertheless, the time required for bacterial indigo reduction is long (2−3 days). Though bacterial indigo reduction is an eco-friendly approach, reproducibility and reduction rates should be improved for application in the industry[11-12].

To find an eco-friendly and safe alternative to SD as a reducing agent in the indigo dyeing processes, some kinds of fruits and their by-products such as apple, banana and persimmon peels were applied as reducing agents in the indigo dyeing process for being eco-sustainable[13-15]. However, the instability of the composition of these materials can cause problems in reduction efficiency.

Some studies used glucose (GS) as a green reducing agent instead of SD in the indigo dyeing process. The aldehyde group of GS can be oxidized to carboxylic acid while indigo is reduced to leuco indigo dyes. GS is successfully employed as a reducing agent for indigo dyeing in alkaline reduction[16-17]. Though GS is eco-friendly, non-toxic, biodegradable and inexpensive, the GS reducing systems need higher temperatures and more alkali to provide the redox potential in the dye bath for indigo.

The reducing activity of thiourea dioxide (TD) is high enough in alkaline aqueous solutions, so it is used as a reducing agent for both organic and inorganic compounds[18]. For example, TD was applied to the discharge printing of polyester fabrics as an effective green reducing agent[19].

Only using TD makes indigo easy to over-reduction. Considering that GS is less reductive, the complex of TD and GS is investigated in this research as green reducing agents to replace SD in the indigo dyeing process on cotton, and the mass ratio of TD to GS is optimized. The studies are performed to evaluate the stability and dyeing properties of the complex reducing agent of TD and GS in indigo dyeing.

1 Materials and Methods

1.1 Materials

Scoured cotton fabrics (165 g/m^2) were purchased from the local fabric market. Synthetic indigo was supplied by Hebi Xingeyuan Denim Technology Co., Ltd., China, and used without further purification. The chemical reagents used were analytical regents, SD (≥ 90%, Tianjin Hengxing Chemical Preparation Co., Ltd., China), TD (≥ 99.0%, Tianjin Chemical Reagent Factory Kaida Chemical Plant, China), GS (≥99%, Tianjin Kemiou Chemical Reagent Co., Ltd., China), NaOH (≥ 96.0%, Tianjin Hengxing Chemical Preparation Co., Ltd., China) and NaCl (≥99.5%, Tianjin Fengchuan Chemical Reagent Co., Ltd., China).

1.2 Stability of indigo reducing solution

The indigo dyeing mother liquor was prepared by adding 1.5 g indigo, 1.5 g NaOH and 1.5 g reducing agent (SD, TD, GS or the complex of TD and GS) in 160 mL water at 60 ℃. Then the indigo mother liquor was diluted to 500 mL to test the reduction potential of the indigo leuco solution. After that, 200 mL indigo leuco solution was added into a tube, then stirred at a rotation speed of 500 r/min on a magnetic stirrer (EYELA Chem. Station PPS-CTRL1, Japan). Reduction potential and pH value were measured at 0, 30, 60, 120 and 210 min, respectively. At the same time, 40 mL indigo leuco solution was taken from the tube to dye cotton fabrics (4 cm ×10 cm) for testing the *K/S* value.

1.3 Dyeing process

The dyeing process is shown in Fig. 2. Dry vat reduction method was used to prepare the dye bath, and then the cotton fabrics were dip-dyed at 25 ℃ for 3 min and oxidized for 5 min with air-oxidation. The bath ratio was 1∶40. The dyed fabrics were washed in distilled water until the water was neutral and then air dried.

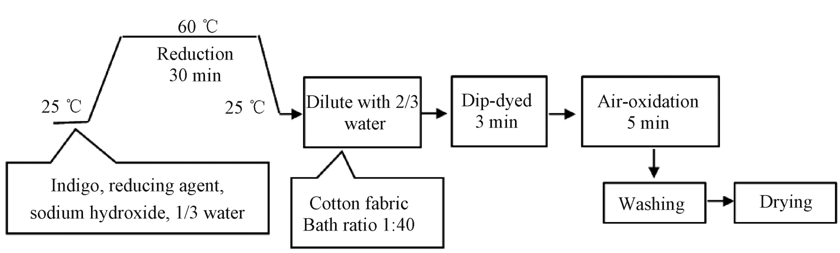

Fig. 2 Dyeing process of indigo on cotton fabrics

1.4 Measurement of reduction potential and pH value

The reduction potential of the reducing dye solution was measured by an oxidation-reduction potentiometer (AZ8551, Heng Xin, China). The pH value was measured by a pH test pen (AZ8686, Heng Xin, China).

1.5 Measurement of chromatic and *K/S* values

The chromatic value of dyed cotton fabric was measured by spectrophotometer (Datacolor International, Switzerland) under illuminant D65 at 10° observer position. The *K/S* value was calculated using the Kubelka-Munk equation

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

where *K* is the absorption coefficient; *S* is the scattering coefficient; *R* is the reflectance.

1.6 Measurement of color fastness

The dyed cotton sample was evaluated for washing fastness according to GB/T 3921—2008 Textiles—test for color fastness—color fastness to washing with soap or soap and soda. The washing test conditions are 2 g/ L sodium carbonate, 2 g/ L soap, 60 ℃, 30 min, liquor ratio of 1∶50. Dry and wet rubbing fastness was measured according to GB/T 3920—2008 Textiles—test for color fastness—color fastness to rubbing. The color fading of the dyed cotton samples and staining on the cotton fabric was assessed by the grey scale method. Level 1 refers to the highest degree of shade fading or staining, while level 5 refers to no shade fading or no staining.

2 Results and Discussion

2.1 Comparison of the reducing agents

The indigo dye bath initially consisted of 3 g/L indigo and 3 g/L NaOH. Then, 3 g/L SD, TD or GS were individually added to the dye bath at 60 ℃ and the reduction reaction of indigo was carried out for 30 min. As shown in Figs. 3 and 4, the reduction potential and the pH value of the indigo leuco solution were recorded with the stirring time. As seen from Fig. 3, with the time of intense stirring, the reduction potential of the three reducing agents all decreases, and that of SD is the most unstable. After 2 h of stirring, indigo cannot be successfully reduced in the production system of SD or GS, whose reduction potential is lower than the data needed in indigo leuco (about − 700 mV[17]), even though the pH value is still higher than 11.0. As shown in Fig. 5, the *K/S* value of the dyed cotton fabrics with TD is the highest in the three reducing agents and relatively stable with the stirring time. The *K/S* value decreases significantly with the stirring time when SD or GS is used as the reducing agent. To replace SD which has an environmental problem, and avoid indigo from being over-reduced, the complex reducing agents of TD and GS are used to improve the stability of the indigo leuco solution.

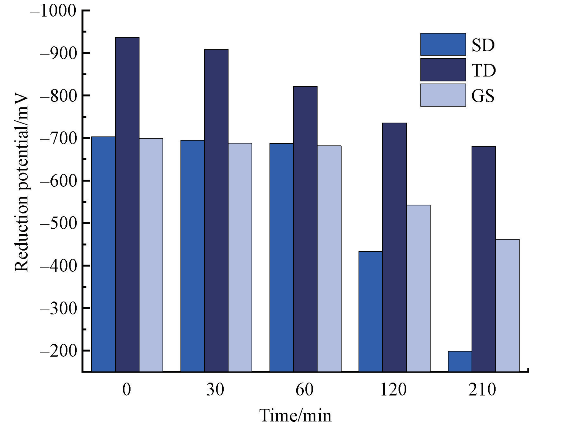

Fig. 3 Changes of reduction potentials in three reducing systems with stirring time

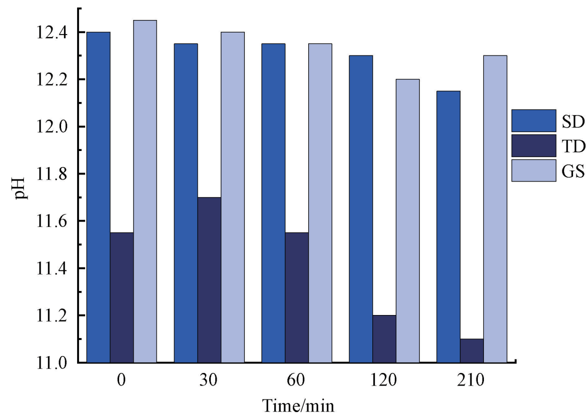

Fig. 4 Changes of pH value in three reducing systems with stirring time

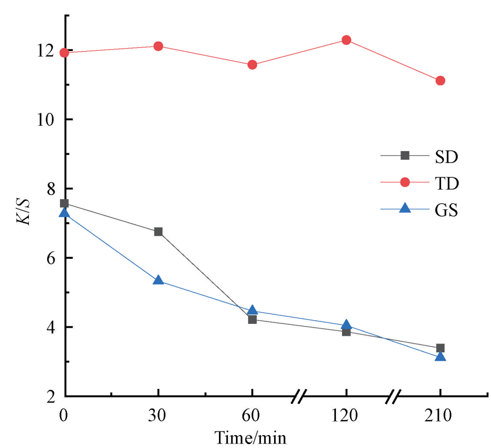

Fig. 5 Changes of *K/S* value of cotton samples in three reducing systems with stirring time

2.2 Effect of TD and GS mass ratio on reduction stability

The reduction potential and pH value of indigo leuco solution with different mass ratios of TD to GS were analyzed. The reduction potentials are shown in Fig. 6. At the beginning of agitation, the reduction potential of the indigo reduction system does not increase obviously with the increase of the mass fraction of TD, but when the mass fraction of TD exceeds 50%, the reduction potential of the indigo reduction system increases obviously and reaches −931 mV on the condition of only using TD. When the mass fraction of TD reaches 90%, the reduction potential is so high that easily causes indigo over-reduction, and it is not conducive to dye. The reduction potential of the indigo reduction system decreases with the increasing of time. When the mass fraction of TD is high, the reduction potential shows a tread of decreasing within 60 min, thus it can not meet the required potential of indigo reduction. When the mass ratio of TD to GS is 7 : 3, the reduction potential changed from −759 mV to −699 mV within 210 min, the range of change is the smallest and the reduction stability is the best in all complex ratios.

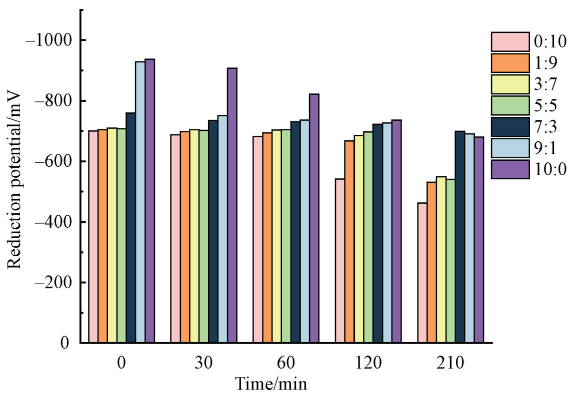

Fig. 6 Changes of reduction potential at different mass ratios of TD to GS with stirring time

The pH values are shown in Fig. 7. When the mass fraction of TD increases, the pH value of the indigo reduction system declines significantly. Since TD produces acid decomposition, the presence of excess TD in turn inevitably increases the amount of alkali used. When the mass fraction of TD exceeds 70%, the pH value declines obviously. Therefore, considering the stability of the pH value, the optimum mass ratio of TD to GS for indigo dyeing is 7 : 3.

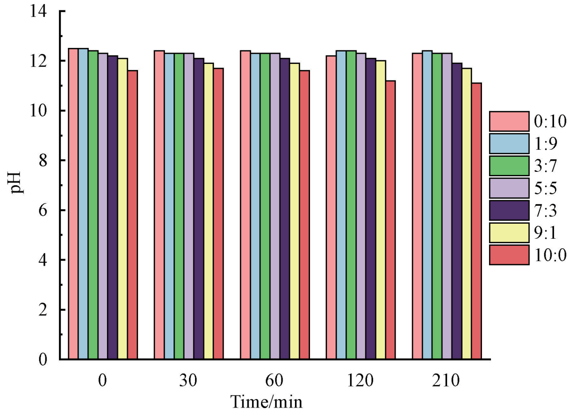

Fig. 7 Changes of pH value at different mass ratios of TD to GS with stirring time

2.3 Effect of TD and GS mass ratio on chromatic values

Cotton samples dyed with different mass ratios of TD to GS (0 : 10, 1 : 9, 3 : 7, 5 : 5, 7 : 3, 9 : 1 and 10 : 0) are named as C−1, C−2, C−3, C−4, C−5, C−6 and C−7, respectively. It can be seen from Fig. 8 that when the mass fraction of TD is lower than 70%, with the increase of TD mass fraction, the *K/S* value of cotton fabrics increased. Since the reduction potential of TD is higher than that of GS, the higher the mass fraction of TD, the fuller the reduction of indigo, and the sodium sulfate produced after the decomposition of TD also plays a role in promoting the dyeing. When the mass ratio of TD to GS is 7 : 3, the surface color depth reaches the maximum. However, the color depth decreases with the further increase of the mass fraction of TD. The reason for this phenomenon is that when the mass fraction of TD is too high, it leads to a high reduction potential of the system. In this case, there is the possibility of over-reduction of indigo, and more di-anion form of leuco indigo is produced, and the directness of indigo to the cotton fiber decreases[5]. With the increase of the mass fraction of TD, it is also clearly found that the maximum absorption wavelength moves to the short-wave direction. When GS is used as the reducing agent, the maximum absorption wavelength is 650 nm; when the mass ratio of TD to GS is 7 : 3, the maximum absorption wavelength is 590 nm. The chromatic values of the dyed cotton samples are shown in Table 1, where L^* is the brightness (0 means black; 100 means white), a^* is the red/green value ($a^* > 0$, indicating a red colour light; $a^* < 0$, indicating a green colour light), and b^* is the yellow/blue value ($b^* > 0$, indicating a yellow colour light; $b^* < 0$, indicating a blue colour light). It can be seen that with the increase of the mass fraction of TD, the value of a^* increases gradually, and reaches the maximum value at the mass ratio of 7 : 3 for TD to GS. The value of b^* decreases, indicates that the blue colour light becomes lighter.

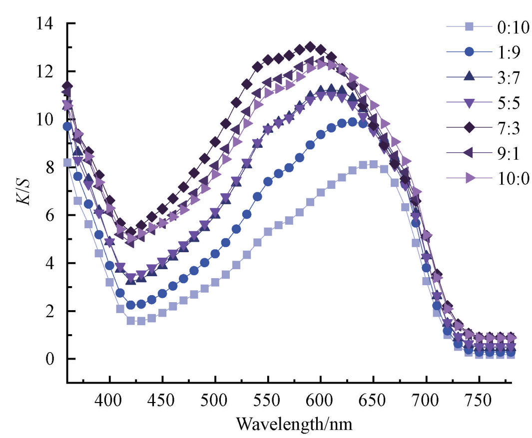

Fig. 8 *K/S* curves of cotton sample with different mass ratios of TD to GS

Table 1 L^*, a^* and b^* values of cotton samples with different mass ratios of TD to GS

Sample	L^*	a^*	b^*	Color block of picture pattern
C-1	35.72	0.44	-21.71	
C-2	31.31	1.11	-20.40	
C-3	27.84	2.12	-17.48	
C-4	27.73	2.10	-16.44	
C-5	24.18	3.56	-12.24	
C-6	25.16	2.50	-12.99	
C-7	25.43	2.16	-12.25	

2.4 Effect of salt on color strength

As can be seen from Fig. 9, the addition of salt (NaCl) promotes the dyeing capacity of indigo. With the increase of NaCl mass concentration, the K/S value of indigo dyeing cotton samples increases at the initial stage. When the mass concentration of NaCl is 10 g/L, the K/S value of the cotton fabric gradually tends to a balance. According to the experimental data, the mass concentration of NaCl with 10 g/L is more suitable.

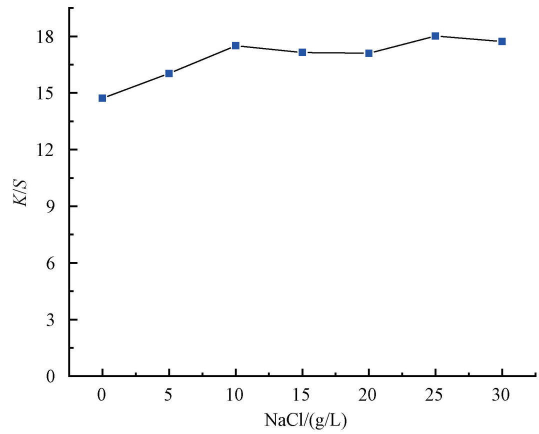

Fig. 9 Changes of K/S values of cotton samples with different mass concentrations of NaCl

2.5 Colour fastness

The cotton samples for color fastness tests are dyed according to Section 2.3 at a mass ratio of 7 : 3 for TD to GS, with 10 g/L NaCl, in the dip dyeing for three times, then soap-boiling (2 g/ L sodium carbonate, 2 g/L soap, 60 ℃, 3 min), washing and drying. After washing, the red light on the surface of the cotton sample is obviously reduced, thus making the blue light of indigo dyed cotton purer and bluer. The chromatic values of the dyed cotton sample are presented in Table 2.

Table 2 Color fastness of indigo dyeing cotton sample

Color block of picture pattern	L^*	a^*	b^*	Washing fastness		Rubbing fastness	
				Fading	Staining	Dry	Wet
	20.69	1.32	-14.81	3-4	4	3	2

According to the method of GB/T 3921—2008 and GB/T 3920—2008, the washing fastness of fading and staining of cotton sample is 3-4 and 4, respectively, and the rubbing fastness of dry and wet is 3 and 2, respectively.

3 Conclusions

In this paper, the stability of three kinds of reducing agents is compared, and it is found that the reduction ability of TD is not only strong but also stable. Although GS is environmentally friendly, its reduction ability is weak and unstable. Through strong-weak recombination, the complex reducing agent of TD and GS not only improves the reduction ability and stability of the dyeing solution, but also solves the problem of indigo over-reduction caused by the strong reduction ability of TD. This method of indigo reduction dyeing works well, and it gives an idea for the use of an environment-friendly reducing agent for indigo dyeing.

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绿色复合还原剂在靛蓝染色中的应用

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摘　要：靛蓝是纺织工业中最重要的还原染料之一，靛蓝染色时，必须在还原剂作用下转化为水溶性隐色体形式。该研究旨在寻找一种复合绿色还原剂，以替代靛蓝染色中使用的对环境不利的连二亚硫酸钠（sodium dithionite，SD）。首先，比较了三种还原剂，SD、二氧化硫脲（thiourea dioxide，TD）和葡萄糖（glucose，GS）的稳定性。采用 TD 作还原剂剧烈搅拌 2 h 仍能保持靛蓝染色所需还原电位，而 SD 和 GS 剧烈搅拌 1 h 达不到靛蓝染色所需的还原电位，靛蓝染色性能下降。鉴于 GS 的环境友好性，选择 TD 与 GS 复合物作为靛蓝染色的复合绿色还原剂。其次，分析复合还原剂不同质量比对棉织物靛蓝染色的还原电位、pH 值和 *K/S* 值的影响。当 TD 与 GS 的质量比为 7∶3，体系具有稳定的还原电位，可获得较好的染色性能。

关键词：靛蓝染色；二氧化硫脲（TD）；葡萄糖（GS）；连二亚硫酸钠（SD）；还原电位；*K/S* 值