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Application of rare earth as mordant for the dyeing of ramie fabrics with natural dyes

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Abstract−Selecting appropriate metallic compounds as mordants is essential for dyeing with natural dyes. This paper presents the application of rare earth compounds as mordant for the dyeing of ramie fabrics with four kinds of natural dyes. The influences of pre-mordanting, simultaneous mordanting, and post-mordanting on the dyeing effect were explored. The post-mordanting was proved to give rise to the highest dye uptake. The effects of dyeing conditions including dyeing temperature and time, dyeing bath pH and the concentration of rare earth on the dye uptake were investigated systematically. The fabrics dyed with natural dyes in presence of rare earth as mordant exhibited high color shade stability in the baths with pH varying from being acidic to neutral and alkaline. Employing rare earth as mordant apparently raised the color fastness to washing, rubbing and light of the ramie fabrics dyed with the natural extracts. In comparison with the commonly used metallic salts, using rare earth chlorides as mordants can greatly reduce the ionic concentration employed in natural dyeing. This study proved that rare earth would be a kind or promising environmentally friendly mordant in natural dyeing.

Key words: Natural Dye, Mordant, Rare Earth, Color Fastness

INTRODUCTION

The colorants used in commercial textile dyeing are almost exclusively synthetic.

However, synthetic dyes not only are harmful to health and but also result in a great deal of environmental pollution [1-6]. As a result, natural dyeing in textiles is now attracting more and more attention from both academia and industry due to its environmentally friendly attributes [1,2,4-16]. Natural dyes can exhibit better biodegradability and generally have a higher compatibility with the environment [3,4,17-19].

Dyeing fabrics with natural dyes often leads to problems such as lower color fastness to washing or light of the dyed textiles [12,14, 20-22]. Most attempts for overcoming these problems involved the use of metallic salts (e.g., aluminum potassium sulfate, potassium dichromate, stannous chloride, ferrous sulfate and copper sulfate) as mordants [3,5,6,9,11-13,23-26]. The metal ions can act as electron donor to form coordination bonds with the dye molecules. The wastewater-containing heavy metal ions from these mordants have significant impact on the environment and public health [25]. The content of heavy-metal ions in textile is limited. Therefore, selecting new mordant to replace traditional heavy-metal ions has been an important part in the development of natural dyeing of textiles.

Rare earths are ecofriendly and compatible with the environment. In general, the coordination number of rare earth can be as large as 8, 9 and even 12 [27,28]. Additionally, the rare earth elements have large atomic radius, which enables a good number of ligands surrounding them [27]. Hence the rare earth ions exhibit high capability for forming coordination compounds with natural dye molecules. As the central ions, the rare earth ions can form coordination bonds with the amino, hydroxyl or carboxyl groups, i.e., the ligands, of the natural dye molecules. When forming coordination compounds with natural dye molecules, the rare earth ions tend to exhibit electrolyte-like effect and thus quickly lower the Zeta electric potential on the surface of fibers. Therefore, they are easily absorbed on the surface of fiber by static electric force. Using rare earth products as mordants can promote the formation of coordination compounds of natural dyes, rare earth and fibers and thus enhance the color fastness of the fabrics dyed with natural extracts.

Our aim here is to study the application of rare earth products as mordant for natural dyeing. The lanthanum-rich rare earth chloride was used as the mordant in the natural dyeing of ramie fabrics. The dyeing conditions including mordanting method, dyeing temperature and time, pH value of dyeing bath and concentration of mordant on the dyeing effect were investigated systematically. The color shade stability of the dyed ramie fabrics with rare earth as mordant was examined in the solutions having different pH values. The effects of using rare earth as mordant on the color fastness to washing, rubbing and light of the ramie fabrics dyed with natural dyes were studied. As compared with conventional metallic mordant ferrous sulfate ($FeSO_4$) and potassium dichromate ($K_2Cr_2O_7$).

EXPERIMENTAL

1. Materials

Ramie plain fabrics (21×21) were used in this study. The fabrics were treated with a solution containing 5 g/*l* non-ionic detergent (Hostapal CV, Clariant) at 50 °C for 30 minutes prior to using. Then the fabrics were thoroughly washed with water and air dried at room temperature for usage. Caesalpinia sappan, Rhizoma coptidis, Garednia and Areca catechu were provided by the Chongqing 3533 Print-

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ing Dyeing and Clothing Co. Ltd. The lanthanum-rich rare earth chloride ($RECl_3 \cdot 6H_2O$) (REO≥50%, La_2O_3/REO=43%, CeO_2/REO =40%, Pr_6O_{11}/REO=5.0%, Nd_2O_3/REO=18%, Sm_2O_3/REO=1.5%, Eu_2O_3/REO=0.2%, Tb_4O_7/REO=0.05%, Non-RE Impurities/REO =2.69%) and neodymium chloride ($NdCl_3 \cdot 6H_2O$) (REO≥50%, Nd_2O_3/REO≥99%, Non-RE Impurities/REO≤1%) were purchased from the Inner Mongolia Baotou Steel Rare-earth (Group) Hi-Tech Co., Ltd. Ferrous sulfate ($FeSO_4 \cdot 7H_2O$) (Analytical Reagent grade, Chengdu Best Reagent Co., Ltd.) and potassium dichromate ($K_2Cr_2O_7$) (Analytical Reagent grade, Chengdu Best Reagent Co., Ltd.) were used as received. Sodium hydroxide, acetic acid and lemon acid of chemical pure grade were purchased as from Sinopharm Chemical Reagent Co., Ltd.

2. Extraction of Natural Dyes

At first, 150 g of a selected plant was precisely weighed with the analytical balance (TE1502S, Sartorius Co., Germany). After being mashed it was put into a big beaker containing 800 ml of water and kept for 24 hours. Afterwards, the mixture was heated to boiling state where it was maintained till up to only 100 ml liquid being left via evaporation. Then the dissolving and evaporating processes were repeated twice. After filtration, the collected colorant liquid was distilled and condensed to 50 ml. The concentrated solution containing the plant extracts was the crude natural dye liquid. The ultraviolet-visible (UV-vis) spectra of the aqueous solutions containing the natural dyes were obtained from U-3310 UV-vis spectrophotometer. As indicated in Table 1, the maximum absorption wave length values of the solutions containing natural dyes range from 410 nm to 460 nm, which are dependent on the different component compositions of the natural dyes. According to the maximum absorption wave length values, it is judged that the major colorant ingredients of the different natural extracts are brazilin of caesalpinia sappan, berberine of rhizoma coptidis, crocin and crocetin of gardenia, and catechin of areca catechu. Fig. 1 illustrates the chemical structure of the major colorant ingredients of the different natural extracts.

Table 1. The maximum absorption wave lengths of the solutions containing natural dyes

	Caesalpinia sappan	Rhizoma coptidis	Gardenia	Areca catechu
Maximum absorption wave length (nm)	412	452	458	458

3. Dyeing

In the dyeing process, a concentrated plant extract liquid was diluted by 10 times and the resultant solution was used as dyeing bath. The

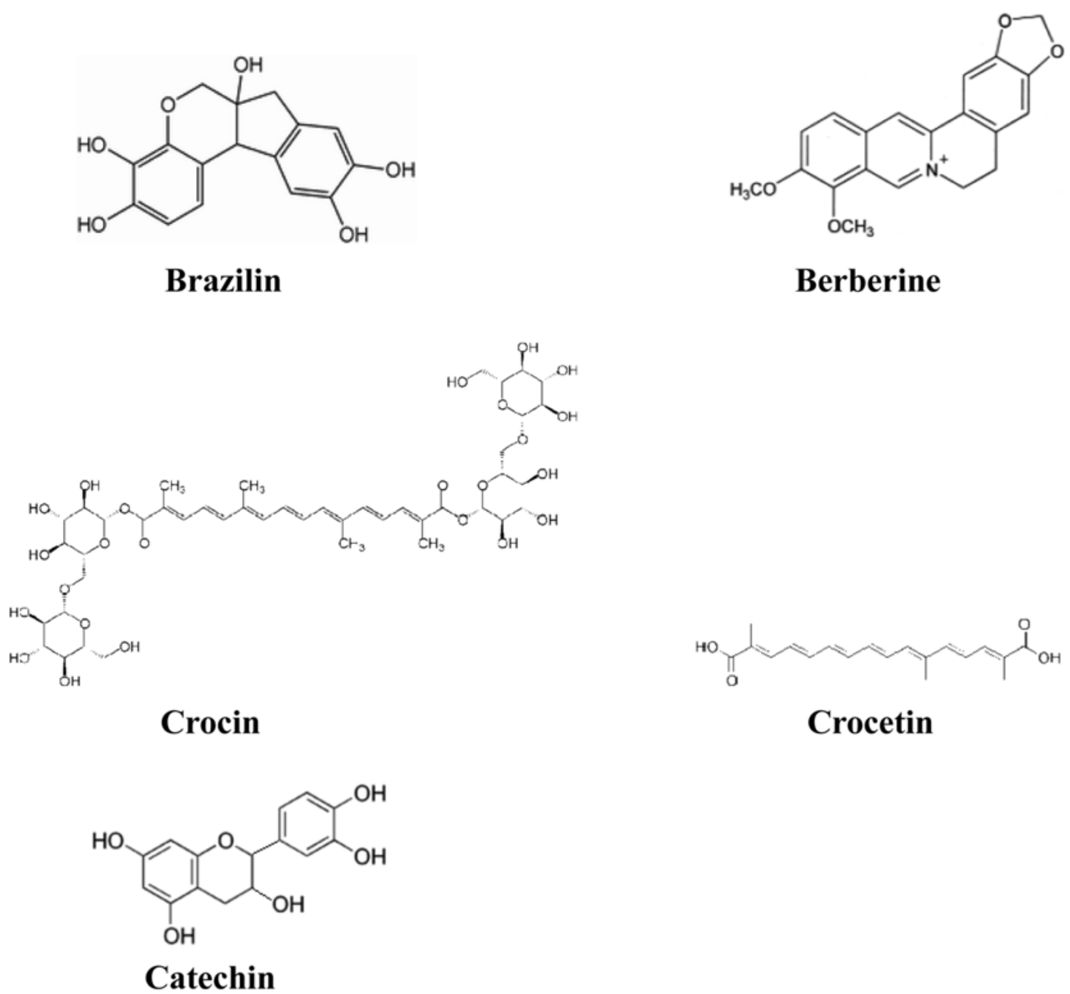

Fig. 1. Chemical structure of the colorant ingredients of different natural extracts.

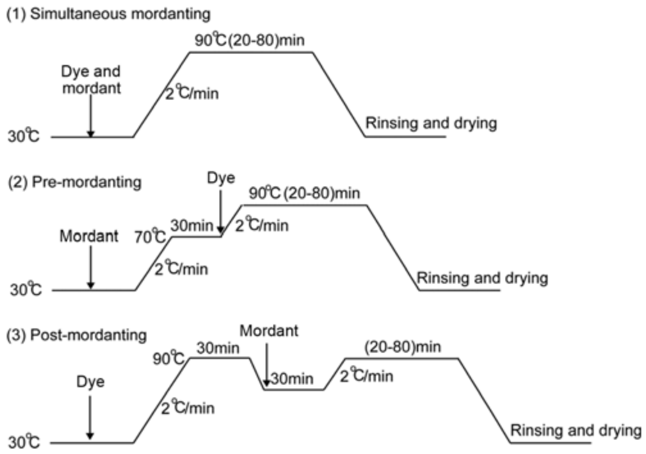

Fig. 2. Different mordanting methods in the natural dyeing.

aqueous extracts were used as a direct dye or with the addition of a mordant. The direct dyeing was carried out by shaking the ramie fabrics with a natural dye solution in a conical flask at 90 ºC in a thermostat shaker bath operated at 100 strokes/min. A material to liquid ratio of 1 : 25 was used in the dyeing experiment. The ramie fabric was then rapidly withdrawn after particular immersion times. After dyeing, the ramie fabric was rinsed with deionized water to remove the unfixed dye and then air dried. The dyeing effect of simultaneous mordanting, pre-mordanting and post-mordanting were compared. Fig. 2 demonstrates the three mordanting methods at the dyeing temperature of 90 ºC.

In the simultaneous mordanting process, the fabrics were immersed in a dyeing bath containing mordant, lemon acid and natural dye at 30 ºC. They the dyeing bath was heated to 90ºC where it was maintained for a particular time (20-80 minutes). The fabrics were then rinsed with clean water at ambient temperature followed by being squeezed and dried. In the pre-mordanting method, the wet fabrics were first immersed in a solution of the mordant and heated to 70 ºC where they were kept for 30 minutes. After being added with the natural dyes the bath was heated to 90 ºC where the fabrics were treated for a particular time (20-80 minutes). Then the dyed samples were rinsed with clean water and dried via the similar processes mentioned above. In the post-mordanting method, the ramie fabrics were first dyed in an aqueous solution containing a natural dye at 90 ºC for 30 minutes followed by being cooled to 70 ºC where the mordant was added. Then the fabrics were kept at 70 ºC for another 30 minutes. Subsequently, the dyeing bath was heated to 90 ºC again where the fabrics were dyed for a time in the range of 20-80 minutes. At last, the fabrics were rinsed and dried. The effects of dyeing temperature and time on the dyeing effect of ramie fabrics with the natural dyes were studied.

4. Measurements

The dye uptake in the dyeing of ramie fabrics was obtained through the measurement of the light absorbances at the wavelength of maximum absorption, of the dye bath before and after dyeing with a U-3310 ultraviolet-visible (UV-vis) spectrophotometer. The dye uptake was calculated with the following equation:

$$\text{Dye uptake} = \frac{A_0 - A_t}{A_0} \times 100\%$$

where A_0 and A_t refer to the absorbances of the dye solutions at the beginning and the end of dyeing, respectively.

The CIELAB colorimetric values including ΔE, L*, a*, b*, C*, and the color strength K/S of the dyed fabrics were measured by DatacolorSF600 Computer Color Matching System (Data Color International) using illuminant D_{65} and 10º standard observer. K/S was calculated from the reflectance values using the Kubelka-Munk equation as follows:

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

Where R represents the reflectance of the dyed fabric and K/S stands for the ratio of the absorption coefficient (K) to scattering coefficient (S). The higher K/S value the greater the color strength.

The color fastness to washing of the ramie fabrics was determined according to the standard ISO 105-C03. The measurement was carried out with both sample and standard ramie fabrics that were sewn together and tested under the same conditions. The sewn fabric was washed at 42 ºC for 30 minutes in a standard soap solution with a material to liquid ratio of 1 : 50. Both fabrics were then separated and rinsed and dried. The color fastness to washing levels, observed against a grey scale, were classified as numbers ranging from 1 and 5, which corresponds to poor to excellent fastness, respectively. Color fastness to dry and wet rubbing of the dyed fabrics was tested according to ISO 105-X12 method. Color fastness to light was tested according to ISO 105-BO2 method. To examine the influence of pH change on the color shade, the fabrics dyed in presence of rare earth as mordant were immersed in the water baths with different pH from 3, 7 to 11 at ambient temperature for 30 minutes. Then the wet fabrics were rinsed and dried for further measurement.

RESULTS AND DISCUSSION

1. Influences of Mordanting Method

The effect of different mordant dyeing methods is shown in Table 2. It was observed that the post-mordanting gave rise to the highest color strength and dye uptake in comparison with simultaneous mordanting and pre-mordanting. In simultaneous mordanting, the colorant molecules and rare earth ions could form insoluble coordination

Table 2. Influences of different mordanting methods

	Caesalpinia sappan		Rhizoma coptidis		Gardenia		Areca catechu	
	K/S	Dye uptake	K/S	Dye uptake	K/S	Dye uptake	K/S	Dye uptake
Simultaneous mordanting	5.25	47.8	6.01	54.6	3.88	39.8	4.98	42.3
Pre-mordanting	5.86	52.2	6.58	60.1	4.23	43.5	5.45	49.8
Post-mordanting	6.12	58.0	7.29	64.1	5.07	48.4	5.96	54.6

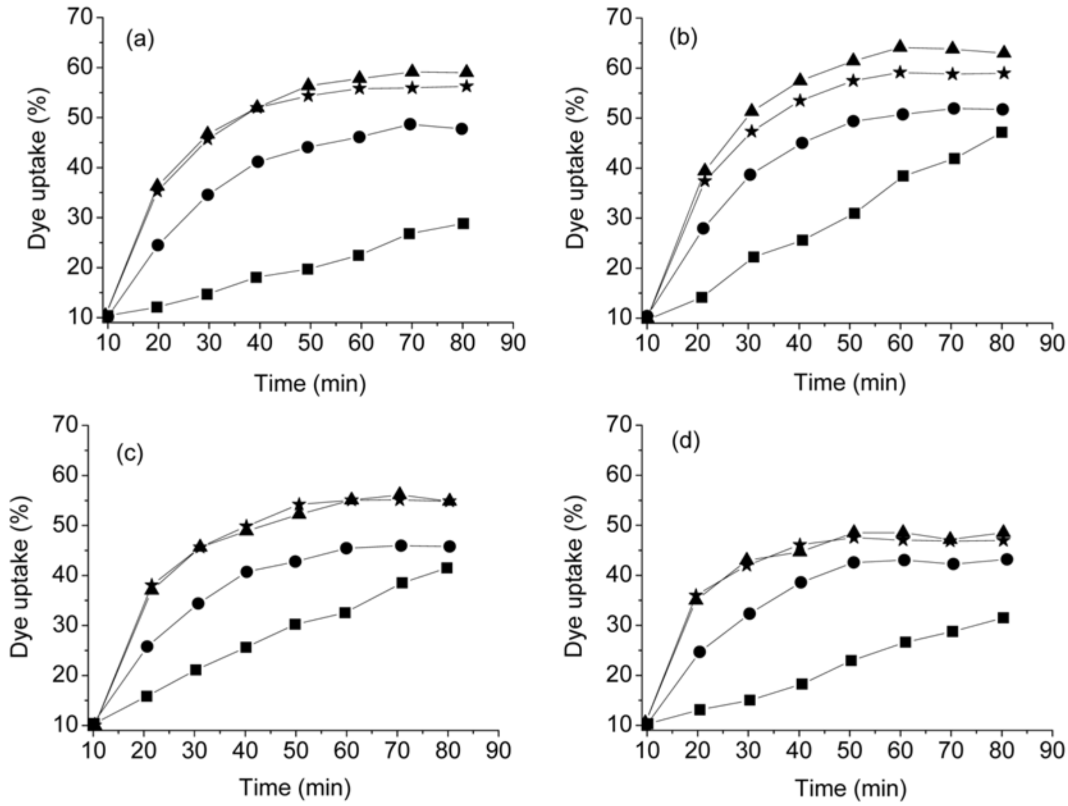

Fig. 3. Influences of dyeing temperature and time on dye uptake: (a) Caesalpinia sappan L; (b) Rhizoma coptidis; (c) Gardenia; (d) Areca catechu. In each plot the symbols refer to different dyeing temperatures. (■) 40 °C; (●) 70 °C; (▲) 90 °C; (★) 105 °C.

compounds and thus precipitated from dyeing bath, resulting in the decrease of effective dye uptake and K/S value, i.e., color strength. In the case of pre-mordanting, the mordant ions absorbed on the fibers could desorb from the fibers and form insoluble coordination compounds with natural dye molecules. Likewise the pre-mordanting resulted in lower color strength. Therefore, the post-mordanting technique was employed in this study.

2. The Optimal Conditions for Dyeing

2-1. Influences of Temperature and Time on Dye Uptake

Fig. 3 presents the influence of dyeing temperature and time on dye uptake. When the dyeing temperature was 40 °C, the dye uptakes of the four kinds of natural dyes increased almost monotonically as the dyeing time rose from 10 to 80 minutes. When the dyeing temperature was 70 °C the dye uptakes of the natural dyes increased rapidly at the beginning. With the extension of dyeing time the increasing tendency of dye uptake decreased gradually. The dye uptakes of the nature dyes were apparently enhanced as the dyeing temperature increased from 70 °C to 90 °C. The increase of dye uptake arises from both the increasing solubility of natural dyes and the expansion of ramie fibers with the increasing temperature. In contrast, the dye uptake of the nature colorants was slightly decreased when the dyeing temperature increased from 90 °C to 105 °C. This is caused by the different temperature dependence of absorption and diffusion of dye molecules. Dyeing takes place in three steps: absorption on the surface of fibers, diffusion to the interior of fibers and desorption from fibers into the dye bath [2]. On the one hand, a lower dyeing temperature is favorable to absorption of the dye molecules on fibers, but makes their diffusion inside fibers difficult. On the other hand, a high temperature leads to expansion of fibers and easy diffusion of natural dyes in fibers accordingly. However a high temperature can also intensify molecular movement resulting in desorption of more dye molecules from fibers. In a word, either excessively low or excessively high temperatures cannot give a desirable dyeing effect. The results show that 90 °C is a suitable temperature for dyeing ramie fabrics with the four kinds of natural dyes. As indicated by Fig. 3, the dye uptake rose gradually with the increase of dyeing time for all the four kinds of natural dyes. When the dyeing time increased to a certain time the dye uptake of a natural dye tended to a constant value, indicating the dye uptake equilibrium was attained [2]. It takes 70, 60, 70 and 50 minutes for the extracts of caesalpinia sappan, rhizoma coptidis, gardenia and areca catechu, respectively, to attain the dye uptake equilibrium, which relies on the molecular size and polarity of the four kinds of natural dyes.

2-2. Influence of pH Value on Dye-uptake

Fig. 4 shows the influence of pH of dyeing bath on the dye uptake in the dyeing with the natural extracts. The figure indicates that the pH change could significantly influence the dye uptake in the dyeing with caesalpinia sappan and areca catechu. When pH value was about 2 the dye uptake of the two kinds of colorants was fairly low. With the increase of pH, the dye uptakes of them rose gradually. When pH value increased the maximum dye uptakes of the extracts of caesalpinia sappan and areca catechu were attained at pH=7 and pH=8, respectively. Afterwards, their dye uptake decreased with the further increase of pH value. The effect of pH on dye uptake can be attributed to the interaction between the natural dyes

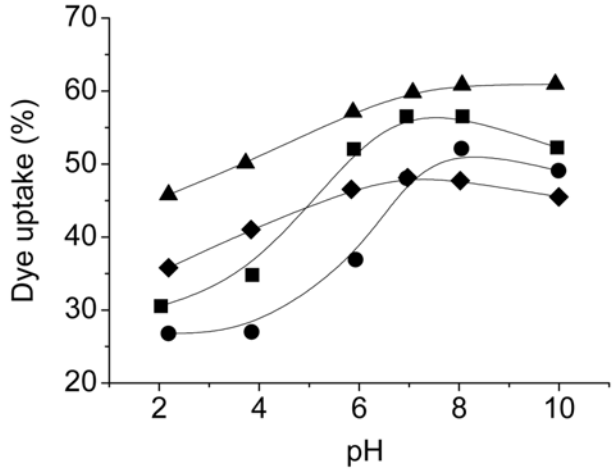

Fig. 4. The influence of pH value on dye-uptake. (■) Caesalpinia sappan L.; (▲) Rhizoma coptidis; (◆) Gardenia; (●) Areca catechu.

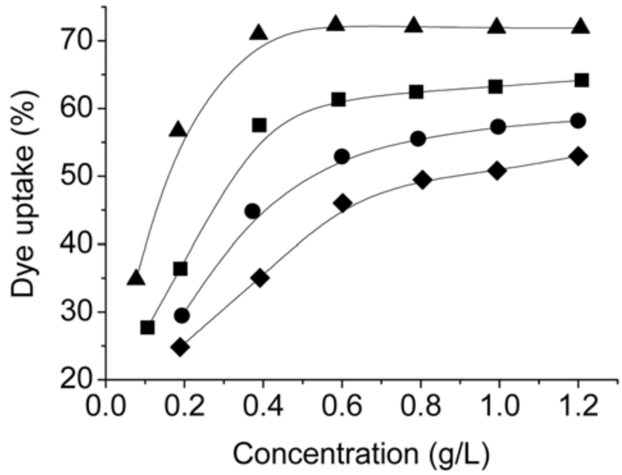

Fig. 5. The influence of the concentration of rare earth on dye-uptake. (■) Caesalpinia sappan; (▲) Rhizoma coptidis; (◆) Gardenia; (●) Areca catechu.

and the ramie fabric. A certain number of OH and COOH groups exist in the cellulose structure. Brazilin and catechin contain polyphenols in their molecules as illustrated in Fig. 1. Increase of pH could promote the ionization of phenolic OH groups resulting in the increase of solubility of the natural dyes in dyeing bath. Hence the dye uptakes of the two natural dyes rose with the increase of pH value. At higher pH, the hydroxyl-ion content increased, and phenolic OH groups in the natural dye molecules and COOH groups in the cellulose fibres were transformed to phenolic oxygen anions and carboxyl anions, respectively. Phenolic oxygen anions had a repulsive interaction with OH groups and carboxyl anions, which prevented the natural dye molecules from being absorbed onto ramie fibers and thus reduced the dye uptakes of the two natural dyes [2]. As one of the major colorant ingredients of gardenia, crocetin contains COOH groups in its molecules. As indicated by Fig. 4, with the increase of pH the dye uptake of the natural extract of gardenia increased, resulting from the increasing solubility of the natural dyes in dye bath due to the ionization of COOH groups in crocetin. Likewise, the dye uptakes of the natural extract of gardenia decreased when pH was above 7 because of the increasing repulsion between the carboxyl anions on natural dye molecules and the carboxyl anions and OH groups on ramie fibers. In comparison with those of caesalpinia sappan and areca catechu, the extract of gardenia exhibited less dye uptake variation with the change of pH because of the relatively low content of COOH groups in the molecules of its major colorant ingredients. With the increase of pH the dye uptake of the extract rose gradually as shown in Fig. 4. As the major colorant ingredient of rhizoma coptidis, berberine is a water soluble dye containing cationic quaternary ammonium salt [9], it would interact ionically with the carboxyl groups of cellulous fibers at higher pH via ion exchange reaction. The number of available anionic sites on ramie fibers in alkaline conditions is relatively larger than that in acidic conditions, and thus the dye uptake of berberine was increased with the dye bath pH.

2-3. Influence of the Amount of Rare Earth on Dye Uptake

The electron configuration of the outer shells of rare earth ions enables them to form complex compounds with the natural dyes and ramie fibers. The influence of mordant amount on the dye uptake is shown in Fig. 5. It can be seen that the dye uptake increased with the increase of the concentration of rare earth. However, when the concentration of rare earth increased to a certain level the dye uptake tended to a constant value because the coordination among natural dye, rare earth and fiber reached to saturation state. The dye uptake of the gardenia extract was the lowest among all the four kinds of natural dyes. This should be due to the low affinity of the crocin and crocetin components in gardenia for ramie fibers. In contrast, the dye uptake of the extract of rhizoma coptidis is the highest, which can be ascribed to the ionic interaction between the cationic dyes and carboxyl anions in ramie fibers. The influence of rare earth concentration on dye uptake of the different natural colorants is determined by their complex formation from rare earth ions and natural dye molecules.

3. Influence of pH on Color Shade of the Dyed Fabrics

It was found that the fabrics dyed with the natural dyes in presence of rare earth as mordant could resist the pH impact and thus change less color shade in washing. To quantify the influence of pH

Table 3. Influence of pH on the colorimetric data of the dyed fabrics

	DE	L*	a*	b*	C*
Caesalpinia sappan (pH=3)	49.89	61.64	3.93	56.98	57.11
Caesalpinia sappan (pH=7)	50.15	60.15	4.26	56.78	56.94
Caesalpinia sappan (pH=11)	51.68	61.38	3.89	55.89	52.03
Rhizoma coptidis (pH=3)	58.98	50.89	5.98	48.61	48.97
Rhizoma coptidis (pH=7)	60.65	50.48	7.03	46.18	46.71
Rhizoma coptidis (pH=11)	59.08	50.90	6.45	49.06	49.48
Gardenia (pH=3)	48.89	82.89	5.58	30.34	30.34
Gardenia (pH=7)	50.15	79.15	5.83	30.86	30.34
Gardenia (pH=11)	54.68	83.68	5.21	32.78	32.78
Areca catechu (pH=3)	38.58	68.08	10.93	41.78	43.19
Areca catechu (pH=7)	40.63	66.65	11.56	40.89	42.49
Areca catechu (pH=11)	39.28	66.98	12.89	40.23	42.24

on color shade, color measurements were performed on the fabrics dyed with the four kinds of natural dyes. L* represents lightness value in the CIELAB colorimetric system. Higher lightness value means lower dye uptake [9,29,30]. a* and b* denote the red/green value and the yellow/blue value, respectively [9,29,30]. The positive values of a* and b* represent redder and yellower while negative shows greener and bluer tones. C* stands for chroma or purity of color [4,9,30]. ΔE refers to color difference [4,9,30]. As shown in Table 3, the colorimetric data including ΔE, L*, a*, b*, and C* of the dyed fabrics did not change much when pH of the bath changed from 3 to 7 and 11. This is ascribed to the formation of stable complexes among rare earth ions, natural dye molecules, ramie fibers. The formation of the coordination bonds is irreversible. The resultant coordination compounds are highly stable in acidic, neutral and alkaline baths. In addition, the multiple complexes formed by rare earth ions and natural dyes can interact with each other, which can result in the dissociation of the electron pairs on the both sides of the complex conjugating system. The dissociated electrons can drift among the complexes and thus generate the so-called ultrasensitive transition effect, which changes the characteristic absorption spectrum. Thus the dyed fabrics can resist the pH fluctuation and maintain stable color shade in either acidic or alkaline bath. This is a significant advantage of using rare earth as mordant in natural dyeing.

4. Color Fastness of the Dyed Fabrics

Table 4 shows the color fastness ratings to washing, rubbing and light of the fabrics dyed with the four kinds of natural dyes in presence and in absence of rare earth as mordant. In comparison with the fabrics colored via direct dyeing, the fabrics dyed having rare earth as mordant exhibited much better color fastness to washing and rubbing. The ratings of color fastness to washing and rubbing of all the dyed fabrics having rare earth as mordant were found to be grade 4-5. The fastness to washing and fastness to rubbing of the fabrics dyed with the natural extracts depend on the type of mordants, mordanting method and mordant concentrations as well as molecular size and chemical structure of the dye, the dye-fiber or dye-fiber-mordant interaction or bonds [7]. The most important factor for determining the color fastness to washing and rubbing is the dye-fiber-mordant interaction, which relies on the formation of stable coordination bonds among rare earth ions and natural dyes and fibers. The ratings of color fastness to light of the dyed fabrics using rare earth as mordant were in the range 3-4 grade. However, the ratings of fastness to light of the dyed fabrics without mordanting were found to be grade 1-2. The color fastness to light of a natural dye is influenced by the chemical structure of dye, physicochemical interaction between natural dye and fiber, physical state of the dye inside the fiber, dye concentration, chemical structure and physical characteristics of the fiber itself, types of mordant, mordant concentrations and mordanting method used [7,12,23]. Generally, it is well known that the color fastness to light of natural dyes was poor [7,23]. In this sense, the light fastness of dyed fabrics with rare earth as mordant is considerably good. The formation of stable coordination bonds between rare earth ions and dye molecules and ramie fibers accounts for the improvement of fastness to light of the dyed fabrics.

5. Comparison of Different Metallic Mordants

As mentioned above, the lanthanum-rich rare earth chloride was proved to greatly improve the color fastness, color strength and dye uptake. Hence it is possible to replace the commonly used heavy metallic salts with the rare earth chloride as the eco-friendly mordant. The authors compared the rare earth mordants with the conventional metallic mordants $FeSO_4$ and $K_2Cr_2O_7$. The efficiency of the different mordants was explored by using $RECl_3 \cdot 6H_2O$, $NdCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$ and $K_2Cr_2O_7$, respectively, as mordants in the natural dyeing of ramie fabrics with Caesalpinia Sappan colorant. Fig. 6 shows the influence of mordant concentration on dye uptake and K/S values in presence of the different mordants. As expected, with the increase of mordant concentration the dye uptake and color strength increased dramatically at lower concentrations, suggesting that all of the mordants can enhance dyeing effect significantly. After a certain mordant concentration level, both the color strength and dye uptake tend to a constant level for all the tests. Combining the dyeing effect together with the consideration of using less metallic mordant, the optimal concentration of $RECl_3 \cdot 6H_2O$, $NdCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$ and $K_2Cr_2O_7$ was determined as 0.6 g/L, 0.6 g/L, 4.0 g/L and 1.6 g/L, respectively. As a result, the ionic concentration employed for deriving optimal dyeing effect was $[Nd^{3+}]$=0.24 mg/L, $[Fe^{2+}]$=0.81 mg/L and $[Cr^{6+}]$=0.57 mg/L. The total rare earth ionic concentration $[RE^{3+}]$ in the $RECl_3$ solution should be close to $[Nd^{3+}]$. Apparently, employing rare earth mordent can greatly reduce the ionic concentration employed in natural dyeing. The coordination number of rare earth elements is larger that that of the Fe^{2+} and Cr^{6+}. The coordination number of d-block transition metals is usually 4 or 6. In contrast, the most common coordination number of rare earth ions is 8 or 9, because when a rare earth ion is coordinated to ligands its 6s, 6p and 5d orbits usually participate in the formation of coordination bonds [27,28]. In addition, the larger ionic

Table 4. Ratings of color fastness of the ramie fabrics dyed with rare earth as mordant

	Washing		Wet rubbing		Dry rubbing		Light
	Fade	Strain	Fade	Strain	Fade	Strain	
Caesalpinia sappan (mordanted)	5	4	3-4	3-4	4-5	4	3-4
Caesalpinia sappan (direct)	3	2-3	2-3	2	3	3	2
Rhizoma coptidis (mordante)	4	4	3-4	4	4	4	3
Rhizoma coptidis (direct)	3	3	2	2	2-3	3	1-2
Gardenia (mordanted)	4-5	4-5	4	3-4	4	5	3-4
Gardenia (direct)	2	2-3	2	2	3	3	2
Areca catechu (mordanted)	4	4-5	4	3-4	4	4-5	3
Areca catechu (direct)	2	3	3	2	3	3	2

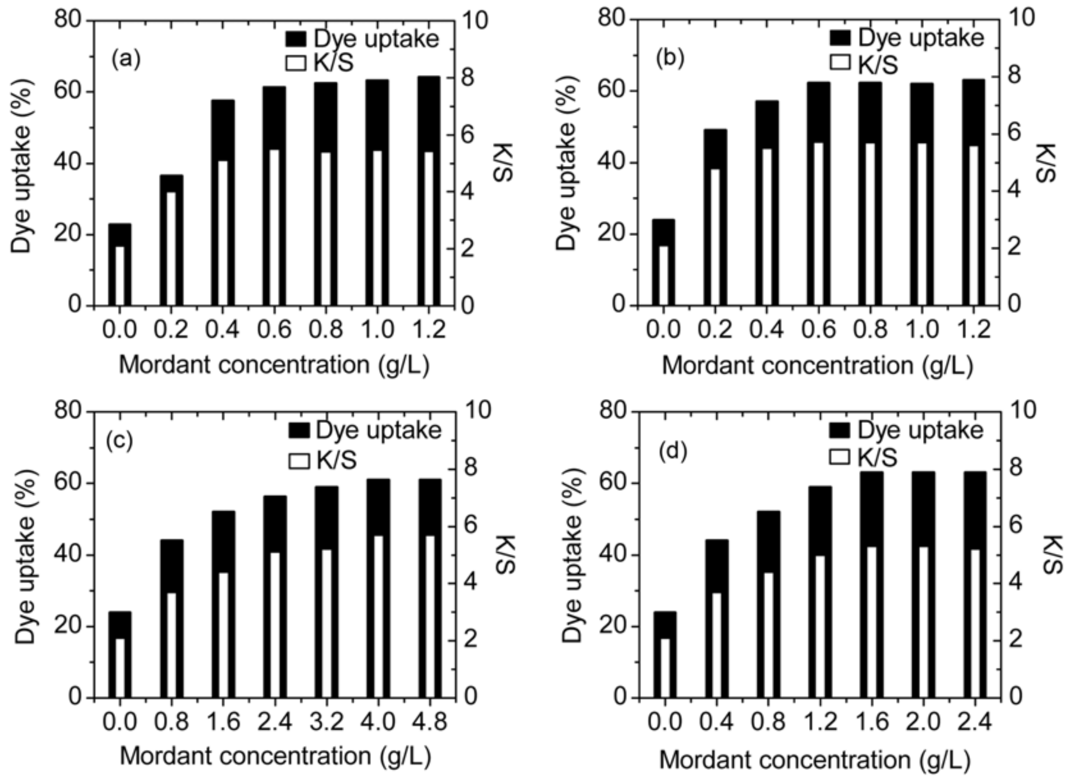

Fig. 6. Influence of mordant concentration of dye uptake and K/S values of the different mordants in the dyeing with Caesalpinia Sappan colorant. (a) $RECl_3 \cdot 6H_2O$; (b) $NdCl_3 \cdot 6H_2O$; (c) $FeSO_4 \cdot 7H_2O$; (d) $K_2Cr_2O_7$.

radius of lanthanide elements accounts of the larger coordination number of rare earth complex. Hence using rare earth chlorides as mordants in natural dyeing can avoid heavy metal pollution. In addition, the presence of metallic mordant usually changes the color shade of dyed fabrics in natural dyeing. For example, Fe^{2+} usually results in the darkening of the dyed fabrics. Using rare earth as mordants can also enlarge the design flexibility in the dyeing process to derive the desired color shade.

CONCLUSION

The rare earth was employed as mordant for the dyeing of ramie fabrics with the natural extracts of caesalpinia sappan, rhizoma coptidis, gardenia and areca catechu. The effects of pre-mordanting, simultaneous mordanting, and post-mordanting on the dyeing effect were compared. The dyeing temperature of 90°C was determined as the best dyeing temperature, while the optimal dyeing time for the four kinds of natural dyes was in the range 50-70 minutes. The highest dye uptake was obtained when the dyeing bath pH was 7 or 8. The fabrics dyed in presence of rare earth as mordant exhibited higher color shade stability. On one hand, this is owing to the stable coordination bonds among the rare earth, natural dye and fiber. On the other hand, it is ascribed to the interaction of the multiple complexes formed by rare earth ions and natural dyes which enable the dyed fabrics to resist pH impact maintaining the constant color shade. It was proved that using rare earth as mordant apparently enhanced the color fastness to washing, rubbing and light of the fabrics dyed with the natural extracts. As compared with the mordants containing Fe^{2+} and Cr^{6+}, the rare earth mordants can greatly reduce the ionic concentration employed in natural dyeing. This study proved that rare earth is promising in the application for mordant in the dyeing with natural colorants.

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