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Dyeing Property of Plant Dyestuffs Used in Cellulosic Fiber Fabrics

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This paper is to research on the dyeing effect of natural plant dyestuffs such as rhubarb and turmeric on cellulosic fiber fabrics by color stripping experiments. The dyeing effects of natural plant dyestuffs used in modified cotton and unmodified cotton is tested respectively by glacial acetic acid stripping extraction experiment, 25% pyridine aqueous extraction experiment, pyridine oxalate extraction experiment and DMF stripping extraction experiment. The unmodified cotton can be completely stripped by glacial acetic acid and 25% pyridine aqueous solution, but they make few effects on modified cotton. There are still some dyes cannot be peeled off on modified cotton by pyridine oxalate solution and DMF stripping experiment. The experiments show that the dyeing effect of natural plant dyestuffs such as turmeric on modified cellulose is better than that on unmodified cellulose.

1. Introduction

In the clothing production process, using plant dyestuffs can reduce the irritation of clothing to the skin with no side nor toxic effects. However, in the actual production process, as the dyeing effect of plant dyestuffs on cellulosic fiber fabrics is relatively poor, the producing department tends to use the modified cotton fiber before dyeing with plant dyestuff to improve the dyeing effects.

2. Literature review

At present, there are many research and application of plant dyes, and many corresponding products have appeared. However, plant dyes are rich in resources, and the recycling of waste plant resources is also worthy of attention. The space for development and utilization is still large. There are few studies on the application of plant dyes in the dyeing of natural cellulose fibers, and the application of dyeing to Lyocell fiber fabrics has not been studied. In particular, studies on the use of natural mordants for plant dyeing of Lyocell fabrics have not been reported. Present study is concerned with the dyeing behavior of gamma irradiated cotton using direct dyes. The fabric and dye powder were exposed to absorbed doses of Cs-137 gamma irradiator between 14 and 26 kGy. It was found that 18 kGy is the optimal absorbed dose for tuning the surface of fabric to get color strength using Direct Yellow 12 (Adeel et al., 2015). In this study, the leaves of the safflower were applied to silk to evaluate the potential for natural staining. Various mordants were used for staining the silk fibers, including copper acetate, aluminum potassium sulfate, sodium tartrate plus citric acid, iron II sulfate, and potassium dichromate. Silk fabric samples were mordanted with alum [KAl(SO4)2.12H2O]. Then, the samples were dyed with cochineal (Dactylopius coccus Costa) and gall oak (Quercus infectoria Olivier) shellac extracts (Yakub et al., 2014). India has conducted more research on the dyeing performance of shellac, not only studied the properties of shellac silk, tussah silk, and wool dyed in shellac, but also studied the properties of dyed cotton in shellac. The cotton is first pretreated with deacetylation chitin to cationize the cotton fibers so that the shellac dyes could be dyed. The dyed fabrics have moderate light fastness, good friction and perspiration fastness, but have poor washing fastness. The washing fastness can be treated with DMDHEU cross-linking or a mordant to improve. The mordant effect of the petal extract of plantain plants is studied. Under the same conditions, the merino wool yarn dyed with turmeric is mordanted with a natural mordant and a chromium mordant (Boudin et al., 2016). The results show that mordants with different concentrations can

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cause different dying effect. 3.5% of the natural mordant and 1.5% of the chromium mordant show similar color fastness, reflectivity, color and K/S values. The natural dyeing of cotton fabrics and silk fabrics without the use of metal mordants was investigated (Yasukawa et al., 2017). Silk and cotton fabrics were dyed using the extract from blackcurrants, and the properties of the dyed fabrics were investigated. The affinity of the extracted dye for the silk fabric was higher compared with that for the cotton fabric. The crystallinity of silk was lower than that of cotton. Indian researchers tried to mordanting the fabrics with a mixture of natural mordants. It was found that mordanting was performed with mixed mordants and that mordants produced a synergistic effect. Compared with the samples using one mordant or different mordants, the mixed mordant mordanted fabric has a comprehensive improvement in performance (Mohini et al., 2018). Later, the researchers studied the properties of mixed mordants consisting of alum and natural mordants. Compared to other metal salts, aluminum salts have low toxicity and are considered the best mordants for the natural dyes. The test found that similar to the natural mixed mordant, the mixed mordant consisting of alum and natural mordant also had a synergistic effect. Indian Y.M. extracted natural plant dyes from phyllanthus reticulatus for cotton fabric dyeing, and studied its dyeing properties and application effects (Economides, 2014). The natural dyes are extracted from the bark of mango and used single or multiple mordants (potassium dichromate, copper sulphate and ferrous sulphate) to pre-dye under optimal conditions. After mordant dyeing and post-mordant dyeing, the effect of different processing techniques on the color fastness was evaluated according to ISO standards (Mcneil et al., 2015). India has also developed dyes made from poplar bark and impatiens, and researched and developed almond dyed yarns, babool dyed nylon and tea dyed wool.

In the present investigation, natural dyes (Mall et al., 2014) from the leaves of Butea monosperma was extracted first time and a range of beautiful shades on cotton fabrics in combination of different mordants were developed. The process of extraction and dyeing is environmental friendly and causes minimum environmental pollution. The dyes extracted can also be utilized for dyeing handloom and craft products for enhancing the livelihood prospects.

In addition, the article “Application and Development Status of Natural Plant Dyes at Home and Abroad” reviewed the pigment classification, dye class, and color of natural vegetable dyes. Methods for extracting natural dyes include conventional water extraction methods, ethanol impregnation methods, ultrasonic methods, dispersant methods, and freeze-drying methods. The dyeing methods of natural dyes include direct dyeing, reducing dyeing, and mordant dyeing. In addition, the study also analyzed the problems of the dyeing of natural dyes, introduced the application and development status and development prospects of natural dyes at home and abroad. In the present study, Terminalia chebula (Myrobalan/Harda) natural dye extract was used for the development of eco-friendly shades on woolen yarn with different hues and tones (Shabbir et al., 2017). The effect of dye concentration on color strength (K/S) of woolen yarn dyed with T. chebula was assessed. The article “Research on Dyeing and Antibacterial Properties of Natural Plant Dyes” gave a classification description of plant dyes, and elaborated the dyeing mechanism, mordant and soaping effects of plant dyes. The dyeing performance of six natural plant dyes such as turmeric, rhubarb, berberine, yellow peony, glutinous rice, and safflower was tested, and the color fastness of dyed fabrics was tested. In addition, the antimicrobial properties of four plant dyes such as turmeric, rhubarb, coptis chinensis (Huanglian) and astragalus were studied. Other scholars pointed out that most plant dyes cannot be separated from the main elemental structures of cellulose C, H, O and M carbohydrates in his article “Dyeing of Chemical Dyes and Plant Dyes”. Plant dye macromolecules are dispersible and can also be regarded as a mixture of complex homologous polymers. The molecular formula can also be written as (C6H10O5) n. Some plant dyes also have a glycoside structure and a certain degree of water solubility.

Through the research background of plant fuels, mordants and lyocell fibers, the optimal dyeing effects of three plant dyes were explored to explore experimentally the application of natural dyes.

3. Principle of experiment

3.1 State of plant dyestuffs in solution

The plant dyes are water soluble and can be made into dye solution. Hydrogen bonds and van der Waals force between dye molecules and ions can make the dyestuffs be aggregated to various degrees. The state of dyestuffs in solution includes ions (D- or D^+), ionic micelles (n Dn^- or n D^{n+}) and micelle {[$(HD)_{mn}$ D] n or $(DA)_{mn}$ D] $^{n+}$}. Under the condition of dyeing, only a single dye molecule or ion, or at most a dye aggregation composed of 2~3 dye molecules or ions can enter the micro gap of the fiber. Therefore, only reducing the aggregation degree of dyestuffs in the dyeing process can enhance the dyeing rate. The aggregation tendency of the dyestuffs is related to the structure of the dyestuff molecules, which have complex structures. large molecular weight, and a conjugated system in the same plane. Molecules contain hydrogen groups and there is no space barrier in the structure, so the aggregation tendency of the dyestuffs will be strong. If there are more water-soluble groups in the dyestuff molecules, the water solubility of molecules will be good and the force between the dyestuffs and the water molecules will be larger. However, after ionizing the dyestuffs take the same charge, which will obstruct the interaction of the dye ions and thus reduce the force among the molecules (ions), and therefore weaken the aggregation tendency. The aggregation tendency of the dyestuffs reflects the attraction between the dyestuff molecules, and to a certain extent also reflects the strength of dye hydrophilic and the attraction between dyestuffs and fibers. Therefore, the aggregation tendency has certain relationship to dyeing properties of dyestuffs.

The main factors affecting the aggregation of dyestuffs include temperature and dyestuff concentration. The aggregation process of dyestuffs in solution is an exothermic process, and low temperature is conducive to aggregation. When the temperature increased, the aggregates will be depolymerized and the aggregation number will be decreased; When the concentration of the dyestuffs in solution is high, the frequency of collision between the dyestuffs are higher, resulting in higher aggregation number, and vice versa.

3.2 State of plant dyestuffs in solution

A successful dyeing process usually consists of 3 stages: adsorption, diffusion and fixation.

3.3 Dyed adsorption isotherm

There are 3 kinds of adsorption isotherms in dyeing: 1. Distribution type adsorption isotherms. The dyestuff concentration on the fibers increased until saturation with the increase of the dyeing solution concentration under the condition of dyeing equilibrium. 2. Freund's adsorption isotherm. The dyestuff concentration on the fiber increases with the rise of that in the solution. 3. Langmuir adsorption isotherm.

3.4 The force between dyestuffs and fibers

The binding force between fibers and dyestuff molecules mainly includes covalent bond force, ionic bond force, van der Waals force, hydrogen bond and valence bond force etc. The combination energy of van der Waals force and hydrogen bond is low, but it plays an important role in the dyeing process because it is the crucial factor for the dyestuffs to be direct to the fiber. The adsorption between van der Waals force and hydrogen bonds is a sort of physical adsorption, which belongs to non-localizing adsorption with a lot of adsorption locations. The energy of combinations of ionic bond, covalent bond, and valence bond is relatively high, and the adsorption caused by these bonds is called chemical absorption or localized adsorption because their adsorption positions in the fibers are fixed.

4. Color stripping experiments

4.1 Experimental materials

According to the optimal processing procedures for dyeing the modified cellulosic fiber directly by turmeric and rhubarb (see Figure 1), this experiment firstly dyes cotton, flax, and several blocks of viscose respectively, which are then soaped for 20 min. The fabric is fully washed to remove the floating color on its surface and is exsiccated for the extraction experiment.

Figure 1: Turmeric dye

Drugs: glacial acetic acid, pyridine solution, oxalic acid, DMF, Zn Cl2, and hydrochloric acid.

4.2 Experimental methods

The glacial acetic acid color stripping extraction experiment

Add 10 mL glacial acetic acid to a 50 mL beaker and heat it to 90 ° C in a water bath. Then add 1g dyed knit fabric, and keep stirring and transfer the stripping solution to the volumetric flask. Repeat until no dye is peeled off and then wash and exsiccate it.

The 25% pyridine aqueous solution extraction experiment

The operation procedures are the same as that of the acetic acid extraction experiment except that the extract liquor used should be 25% pyridine aqueous solution.

The pyridine oxalate color stripping extraction experiment

Take 0.03g dyed sample in a 50ml beaker and add 10ml pyridine and 1g oxalic acid, and then peel off the color in the water bath at 90 ° C for a period of time. Transfer the stripping solution to a volumetric flask and dissolve the solid oxalic acid left in the test tube with a small amount of distilled water. Then transfer it to the volumetric flask. Repeat the operation until no dye can be peeled off. Finally wash and exsiccate it.

The DMF color stripping extraction experiment

Add 27.5 g Zn Cl2 and 17 ml 36% concentrated hydrochloric acid respectively in 500 ml DMF, and stir it to obtain the extract liquor with pH 4. The operation procedures are the same as that of glacial acetic acid extraction experiment, except that the extract liquor should be DMF.

5. Experimental results

5.1 The combination of turmeric and modified cellulosic fibers

The stripping experimental results of turmeric dyestuffs are shown in Table 1. Taking the results of unmodified and modified cotton dyeing contrast as an example, it is found that flax and viscose fiber results are the same as that of the cotton fiber, so they are omitted here.

Table 1: Turmeric dye stripping experiment

raw material	Glacial acetic acid stripping	25% aqueous pyridine solution color stripping	Pyridine oxalate stripping	
Unmodified cotton	Completely stripping	Completely stripping		Unmodified cotton
Modified cotton	A small amount of color stripping	A small amount of color stripping	Completely stripping	Modified cotton

As can be seen from Table 1, the color of unmodified cotton fabric dyed by turmeric is completely stripped through glacial acetic acid and 25% pyridine aqueous solution stripping experiments, indicating that no ionic bond or covalent bond is formed between the turmeric dyestuffs and the cotton fiber and the bonding between them is weak. However, the modified cotton fabric dyed by turmeric is stripped with only a small amount through the stripping experiments, indicating that ionic bond or covalent bond is formed. The fact that ionic bond is formed between turmeric dyestuffs and modified cotton fiber is proved by pyridine oxalate color stripping experiment. Pyridine oxalate is more polar than pyridine aqueous solution. It can peel off the dyestuffs with strong binding force from the fiber, which shows that the binding force between modified cotton and turmeric dyestuffs is stronger than that between unmodified cotton and turmeric dyestuffs. It can be inferred that the binding process between the natural plant dyestuff turmeric and the modified cotton is as follows: the hydroxyl of the dyestuff is ionized in the aqueous solution to generate the oxygen anion, which is ionically bonded with the quaternary ammonium dye base of the modified cotton; Meanwhile, since the turmeric dyestuff molecular structure is linear with the same plane and the dye molecular structure contains hydroxyl, the turmeric dyestuff can be combined with cellulosic molecules by combining the van der Waals force and the hydrogen bond. The binding force between the turmeric dyestuff and the cellulosic fiber can also explain the color change of unmodified cotton before and after soaping during the dyeing process with turmeric dyestuff. As the turmeric dyestuff has good directness, when they are used for the unmodified cellulosic fiber dyeing, the value of color aberration of the dyed fiber is very high but the value drops dramatically after soaping. Therefore, the bindings force between the turmeric dyestuff and the unmodified cellulose fibers mainly includes hydrogen bond and van der Waals force. The combination of the two is shown in Figure 2.

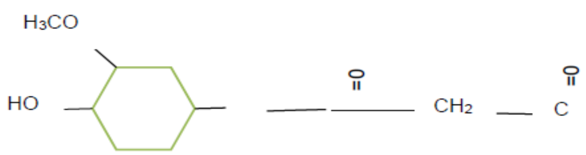

Figure 2: The combined shape of turmeric and unmodified cellulosic fibers

After the modification of the cellulosic fiber, the molecule contains quaternary ammonium group N+R3, which enables the fiber taking a positive charge in the aqueous solution and generating a charge attraction with the negatively charged dyestuff, forming ionic bonds. Therefore, in addition to the hydrogen bonds and the Van der Waals forces, ionic bond with strong binding force is also formed between the turmeric dyestuff and the modified cellulosic fiber. The combination of the two is shown in Figure 3.

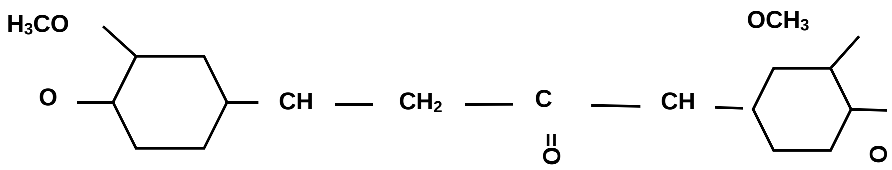

Figure 3: Turmeric dyestuff and modified cellulosic fiber combination

5.2 The combination of rhubarb and the modified cellulosic fibers

The results of rhubarb dyestuff color stripping experiment are shown in Table 2.
As can be seen from Table 2, through glacial acetic acid and 25% pyridine aqueous solution stripping experiments, only a small amount of color of modified cotton was stripped, indicating that the ionic bond or covalent bond is formed between turmeric dyestuffs and modified cotton fibers. Through the pyridine oxalate solution stripping experiment, some dyes of the modified cotton still not be peeled off, indicating that the binding force between the rhubarb dyestuff and the modified cotton includes not only ionic bond. The DMF color stripping extraction experiment is done to further verify the binding force between the two. After DMF stripping, there is still some dyes on the modified cotton left, indicating that covalent bond is formed between the rhubarb dyestuff and the modified cotton. Therefore, it can be inferred that the binding process between the natural plant dyestuff rhubarb and the modified cotton is as follows: the hydroxyl of the dyestuffs is ionized in the aqueous solution to generate oxygen anion, which is ionically bonded with the quaternary ammonium dye base of the modified cotton; Meanwhile, as the rhubarb dyestuff molecules may contain carboxyl (parietic acid), carboxyl will react with the hydroxyl in cellulose and generate ester groups, in which process the two combined in the form of covalent bond. In addition, rhubarb dyestuff can also combine with cellulosic molecules in the form of the van der Waals forces and the hydrogen bond. The conclusions above can also be concluded from the experiments on flax and viscose fabrics.

Table 2: Rhubarb dyestuff stripping experiment

raw material	Glacial acetic acid stripping	25% aqueous pyridine solution color stripping	Pyridine oxalate stripping	DMF stripping
Modified cotton	A small amount of color stripping	A small amount of color stripping	Completely stripping	Completely stripping

In short, after the modification of the cellulosic fiber, the molecule contains quaternary ammonium group N+R3, which enables the fiber taking a positive charge in the aqueous solution and generating a charge attraction with the negatively charged dyestuff to form an ionic bond. Therefore, in addition to the hydrogen bonds and the Van der Waals forces, ionic and covalent bonds with strong force are also formed between rhubarb dyestuff and modified cellulose, in which ionic bonds make up the major part. The combination of the two is shown in Figure 4.

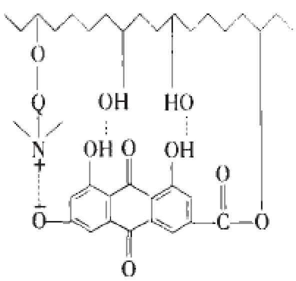

Figure 4: Yellow and modified cellulosic fiber bonding state

6. Conclusions

According to the experiment of turmeric dyestuff and modified cellulosic fiber, the use of glacial acetic acid and 25% pyridine aqueous solution color stripping on the unmodified cotton can completely accomplish the color stripping, while on the modified cotton there is only a small amount of color can be stripped. According to the experimental results of the combining state of rhubarb and modified cellulosic fiber, no effective covalent bonds or ionic bonds are formed between the unmodified fiber and the turmeric dyestuff; While between modified cotton and turmeric dyestuff, there are not only covalent and ionic bonds formed, but also hydrogen bonds and the Van der Waals forces. Besides, rhubarb dyestuff may contain antelope itself, which can chemically react with cellulose to form ester groups in the form of covalent bonds. In short, plant dyestuff such as turmeric have a better dyeing effect on the modified cellulose than on unmodified cellulose.

With the continuous development of social economy, people are more and more demanding on clothing. Apparel fabrics, breathability, dyes and the like have gradually become the consideration of consumers to choose clothes. People are not only pursuing the clothing designs, but also paying more attention to the overall quality. Therefore, garment manufacturers should attach great importance to the quality of garment dyestuffs all the time.

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