Dyeing properties of cashmere fiber dyed with gardenia blue pigment

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Abstract: In the historical road of human mining natural dyes, "plant dyeing" occupies a considerable part. Plant dyes are from nature and used for environmental protection, so they have high development value. In this paper, the dyeing properties of cashmere dyed with gardenia blue pigment were studied. Through orthogonal test and single factor analysis, the effects of pH value, reaction temperature, dye mass fraction and reaction time on color characteristic value and color fastness were investigated. The optimum direct dyeing process of gardenia blue on cashmere fiber was determined as follows: pH value of dye solution is 4.0 - 4.5, dye mass fraction is 7.5% o.w.f, temperature is 75 ℃, time is 50mins, bath ratio is 1:30. Direct dyeing and mordant dyeing were used to dye gardenia blue on cashmere fiber. The results show that different blue effects can be dyed by different mordants. When ferrous sulfate was used as mordant, the dyeing depth increased, but the color became gray. When copper sulfate is used as mordant, the dyeing depth increases and the color light changes most obviously due to the influence of copper ions.

CLC No: TS 194.1 Document identification code: A

1 Introduction
With the enhancement of people's awareness of environmental protection and the implementation of environmental protection laws and regulations in various countries, although synthetic dyes have the advantages of bright colors and low price, they are more and more controversial because of the harmful substances produced in the production process to human body and environment. Natural plant dyestuffs are favored by the world for their natural environmental protection, antibacterial and easy degradation. At the same time, China is a big textile trade country in the world, and the output of cashmere ranks first in the world. However, in recent years, it has received the green trade barrier of WTO, which hinders the development of China's advantageous cashmere industry. To break the green trade barrier, we must take the road of environmental protection and energy saving dyeing and processing, combine the natural and environmental friendly plant dyes with new technologies, and develop new cashmere products with high added value that conform to the modern trend [1].

"Blue dyeing" has always been the most popular and commonly used dyeing method in plant dye, and green and purple are also made from blue overprint. However, among many plant dyes, natural blue pigment is rarely found in nature. Indigo is mainly extracted from various bluegrass such as Polygonum,
Isatis indigotica, and acanthaceous indigo for dyeing, but Indigo is vat dyeing. Generally, it is not suitable for cashmere dyeing. Therefore, this paper selects the natural blue dye—Gardenia blue pigment. It is a dark blue powder with gardenia fruit as raw material. It is soluble in water and has bright blue color. Gardenia blue pigment has good solubility and strong coloring power. Common metal ions, acids and bases have no effect on its color. At the same time, it has good heat resistance. Therefore, it can replace the chemically synthesized blue pigment. Compared with synthetic pigments such as brilliant blue and indigo, it is a natural pigment with good compatibility and high safety.

At the same time, Gardenia jasminoides is a kind of ornamental, edible and medicinal plant with high development and utilization value. Gardenia blue pigment, as a pigment extracted from gardenia fruit, has the effects of anti-inflammatory, analgesic, anti-tumor, prevention and treatment of influenza. This paper will study the dyeing effect of this dye on cashmere fiber. Firstly, through orthogonal analysis and single factor experiment, select representative influencing factors and the best process for direct dyeing, and then compare the effect of the mordant and its dosage and time on dyeing.

## 2 Experimental part

### 2.1 Experimental materials and instruments

Materials: 100% Cashmere (16.12 μm, 31.3 mm), formic acid, ferrous sulfate, aluminum potassium sulfate, copper sulfate are all analytical pure (purchased from Tongxiang Zhenhe Chemical Instrument Co., Ltd.), gardenia blue pigment (Henan Zhongda Hengyuan Biotechnology Co., Ltd.), leveling agent (Shanghai Yayun Textile Auxiliaries Co., Ltd.), soap tablet (Shanghai Textile Industry Technical Supervision Institute), artificial sweat liquid.

Instruments: electronic balance, exact portable spectrophotometer, HG-TC100B constant temperature oscillation water bath pan, Y802N eight basket constant temperature oven, Datacolor 850 color measuring and matching instrument, Y571N dyeing rubbing fastness machine, Y902-II perspiration color fastness machine, SW-8A wash color fastness machine.

### 2.2 Experimental method

In the experiment, two kinds of dyeing processes were used for dyeing with plant dyes, the influence of different dyeing processes on the dyeing effect of cashmere fiber was discussed, and the dyeing indexes were compared and analyzed.

**2.2.1 direct dye**. Dyeing recipes: Dye dosage: 3-9% o.w.f, bath ratio 1:30.

Dyeing process: dissolving the dye powder at 40-50 °C → adjusting the dyeing solution to the specified pH value → dyeing fiber, heating to the specified temperature → constant temperature heating and timing → washing and soaping (soaping temperature is 60 °C, time is10mins) → oven drying.

**2.2.2 mordant dyeing**. The experiment was carried out using metachrome process, which mixed the mordant in the pigment solution for dyeing. The mordant can interact with the dye molecules to make the dye molecules firmly adsorb on the fiber, thereby allowing the fiber to develop color.

Dyeing recipes: mordant (ferrous sulfate) dosage 3-9% (o.w.f), dyeing powder dosage 7.5%, leveling agent 3% o.w.f, bath ratio 1:30.

Dyeing process: Dye powder and mordant dissolve at 40-50°C to no particles → adjust the dye solution to the specified pH value → fiber enters and heat to the specified temperature → constant temperature heating and timing → washing, soaping (soaping temperature 60°C, Time 10mins) → oven drying.
2.3 Testing indicators

2.3.1 color characteristic value. Using D65 light source and 10 ° observation angle, the color characteristic values L *, a *, b *, c *, and K/S values were determined by using the computer color measuring and matching system of datacolor850. L * represents the lightness value; a * represents the red or green value (+ a *: reddish; - a *: greenish); b * represents the yellowish or blue value (+ b *: yellowish; - b *: bluish), and c * represents the chromaticity value. The higher the value is, the purer the color is. K/S is the color depth, and the higher the value is, the darker the color is.

2.3.2 color fastness to soaping. According to GB / T 3921-2008 《Textile – Tests for color fastness to soaping》, the color fastness grade of color change and lining fabric was evaluated by grey sample card and staining card under D65 light source.

2.3.3 color fastness to rubbing. According to GB / T 3920-2008 《Textile – Tests for color fastness to rubbing》, the dyed wool sample is tightly wound on the standard size white cardboard and placed on the friction fastness tester for testing. The dry and wet rubbing fastness of the samples was evaluated by staining card under D65 light source.

2.3.4 color fastness to perspiration. According to GB / T 3922-2013 《Textile – Tests for color fastness to perspiration》, and use perspiration color fastness oven.

3 Results and discussion

3.1 direct dyeing experiment of Gardenia Pigment

3.1.1 orthogonal optimization experiment and range analysis. In order to explore the influence order of dyeing factors on cashmere dyeing with gardenia dyes, the orthogonal optimization method was used. Four factors including dye dosage, dyeing time, dyeing temperature and pH value were selected, and three levels of each factor were selected for L9 (34) orthogonal test. The experimental results are shown in Table 1.

| Serial number | Dye mass fraction/% | Dyeing time/mins | Dyeing temperature/°C | Ph value | C value | K/S value |
|---------------|---------------------|------------------|-----------------------|----------|---------|-----------|
| 1             | 3                   | 40               | 50                    | 3        | 8.35    | 0.60      |
| 2             | 3                   | 50               | 75                    | 4        | 10.67   | 1.28      |
| 3             | 3                   | 60               | 90                    | 5        | 9.99    | 0.40      |
| 4             | 6                   | 40               | 75                    | 5        | 7.55    | 0.25      |
| 5             | 6                   | 50               | 90                    | 3        | 10.71   | 2.89      |
| 6             | 6                   | 60               | 50                    | 4        | 11.14   | 0.40      |
| 7             | 9                   | 40               | 90                    | 4        | 11.93   | 3.32      |
| 8             | 9                   | 50               | 50                    | 5        | 9.90    | 0.19      |
| 9             | 9                   | 60               | 75                    | 3        | 12.73   | 2.47      |

C value K1 9.67 9.28 9.80 10.60
According to range analysis, the order of the factors to dyeing depth K / S value is reaction temperature > pH value > dye mass fraction > reaction time; for color saturation C, the order is: pH value > dyeing time > dye mass fraction. The K/S value of dyeing depth first increases and then decreases with the dyeing time. With the reaction going on, the dye adsorption reaches saturation. In the whole dyeing process, there will be a desorption process. If the reaction time is too long, the degree of desorption will increase. The dye can only be adsorbed on the surface of the fiber, which reduces the utilization of the dye.

In conclusion, the pH value, reaction temperature and dye dosage have significant effects on the dyeing effect, so single factor analysis experiment is carried out for these three factors.

3.1.2 Single factor analysis

3.1.2.1 pH value. Choose the pH value of 2, 3, 4, 5, 6 and other conditions: dye dosage is 6% o.w.f, dyeing time is 50 mins, temperature is 75°C, bath ratio is 1:30. The cashmere fiber was dyed, and its color characteristic value was tested. The experimental results are shown in Figure 2.

The analysis shows that as the pH of the dye solution increases, the C value first increases and then decreases, and the K/S value gradually decreases. This is because the gardenia blue pigment is negatively charged, and the isoelectric point of cashmere is about 6.5. When the pH value is lower than the isoelectric point, the cashmere is positively charged and generates electrostatic attraction between the dye and the dye's adsorption capacity to wool increase. However, if pH value lower than 2.0, it will significantly increase the damage of the wool, resulting in a decrease in strength, and poor gloss affecting the subsequent spinning process. In summary, the pH value of 4 for dyeing cashmere fiber with gardenia blue pigment is better.
3.1.2.2 Dye temperature. Choose the dye temperature of 50, 75, 90°C. Other conditions are: dye dosage is 7.5% o.w.f, dyeing time is 50mins, dye solution Ph is 4, bath ratio is 1:30, dye cashmere fiber, test its color characteristic value, the experimental result is shown in Figure 2.

Fig.2 Single factor experiment of direct dyeing — Dye temperature

The analysis shows that as the dye reaction temperature increases, the C value and K/S value first increase and then decrease. This is because as the temperature increases, the kinetic energy of the dye increases, the puffing degree of cashmere is larger, and the dyeing saturation increases, which is conducive to dyeing. At the same time, the scaly layer is also a highly cross-linked area, and the increase in temperature can change the force between molecular chains or combine side chain groups to increase the rate of dye absorption. However, if the temperature is too high, some dyes will be destroyed and the structure of cashmere will be damaged, which will make the dyeing effect worse. If the temperature is too low, the dyeing depth will be different and the surface will be colored. In summary, the best dye temperature for dyeing cashmere fiber with gardenia blue pigment is 75°C.

3.1.2.3 Dye dosage. Select the dye dosage of 3, 4.5, 6, 7.5, 9% o.w.f. Other conditions are: pH value is 4, dyeing time is 50mins, temperature is 75°C, bath ratio is 1:30, dyeing cashmere fiber, testing its color characteristic value, the experimental result is shown in Figure 3.

Fig.3 Single factor experiment of direct dyeing — Dye dosage

The analysis shows that as the mass fraction of gardenia dye increases, the C value first increases and then decreases, and the K/S value gradually increases. When the amount of dye reaches 7.5% o.w.f, the C value is the largest. This is because after the dye dosage reaches saturation, the degree of dye aggregation in the solution is large, and the dye is easily salted out by the electrolyte, and the degree of
dyeing is lower. At the same time, considering the solubility of dyes in water and the relatively expensive cost of plant dyes, it is better to dye cashmere fibers with gardenia blue pigment with a dye dosage of 7.5% o.w.f.

Comprehensive orthogonal optimization experiment and single factor experiment analysis, it can be concluded that the best dyeing process of gardenia pigment is as follows: Ph value is 4, dye dosage is 7.5% o.w.f, temperature is 75°C, time is 50mins, bath ratio is 1:30.

3.2 Mordant dyeing experiment with gardenia pigment

3.2.1 The influence of mordant and its dosage on dyeing. The formation of coordination bonds among the mordant, dye, and fiber helps to improve the color fastness. At the same time, the mordant has a certain color enhancement effect on the cashmere fiber dyed with gardenia pigment. However, as the concentration of the mordant is too large, the color enhancement effect of dyed fibers is not obvious [2], and the hue after mordant dyeing may change, so the following research is done.

Three common mordants, ferrous sulfate, aluminum potassium sulfate, and copper sulfate were used in the experiment. According to the mordant dyeing process in section 1.2.2, the cashmere fiber was dyed. The effect of mordant and its dosage on the color of dyed fiber was investigated. The results are shown in Figure 4.

Fig. 4 Single-factor experiment of mordant dyeing — mordant dosage

The analysis shows that when copper sulfate and potassium aluminum sulfate are mordant, the K/S value gradually increases as the mass fraction of mordant increases. When ferrous sulfate mordant dyes, the K/S value first increases and then decreases with the increase of the mordant mass fraction. The reason may be that the dyeing interaction of copper sulfate mordant reaches saturation at 6% o.w.f. But there is also the possibility of uneven dyeing.

3.2.2 Mordant temperature. The dosage of ferrous sulfate, potassium aluminum sulfate and copper sulfate are selected as 6% o.w.f, and the same mordant dyeing is carried out in accordance with section 1.2.2 and the best dyeing process. The influence of mordant dyeing temperature on the K/S value of cashmere fiber is shown in Figure 5.

Fig. 5 Single-factor experiment of mordant dyeing — mordant temperature
3.3 Comparison of color characteristic values and color fastness between direct dyeing and mordant dyeing

According to the mordant dyeing process and the best dyeing process in section 1.2.2, the color characteristic value and color fastness of cashmere fiber dyed by direct dyeing and three kinds of mordant dyeing were compared. The results are shown in Table 2.

| mordant          | None (Direct dye) | ferrous sulfate | aluminum potassium sulfate | copper sulfate |
|------------------|-------------------|----------------|-----------------------------|----------------|
| Color characteristic value | L     | 46.91 | 42.44 | 47.64 | 38.49 |
|                   | a*    | -8.2  | -9.14 | -9.02 | -10.42 |
|                   | b*    | 5.73  | 2.09 | 4.42 | 1 |
|                   | c*    | 11.92 | 10.93 | 10.75 | 11.44 |
|                   | k/s   | 2.91  | 4.2 | 2.91 | 5.86 |
| color fastness to soaping | wool staining | 3-4 | 3-4 | 4 | 4 |
|                   | cotton staining | 4-5 | 4-5 | 4-5 | 5 |
| color fastness to rubbing | dye rubbing | 4-5 | 4-5 | 4-5 | 4-5 |
|                   | wet rubbing | 4-5 | 4 | 4-5 | 4 |
| color fastness to perspiration | discolour | 3 | 3-4 | 4 | 3-4 |
|                   | wool staining | 3-4 | 4 | 4 | 4-5 |
|                   | cotton staining | 4 | 4-5 | 4-5 | 5 |
|                   | discolour | 3-4 | 3-4 | 4 | 4-3 |
|                   | wool staining | 3-4 | 3-4 | 4-5 | 4 |
|                   | cotton staining | 3-4 | 4-5 | 4-5 | 4-5 |

Mordant experiment analysis: K/S value gradually increases with the rise of mordant temperature. However, when the ferrous sulfate is mordant, the K/S value rises more with the increase of temperature, and the other two are similar.
The experimental data obtained: the $a^*$ value of the gardenia blue pigment direct dyeing fabric and the mordant dyeing fabric are negative, and the absolute value is large. At the same time, the $b^*$ value is positive, but the absolute value is small, indicating that the dyeing color is blue-green with a yellow tone.

The mordant affects the color characteristic value of dyeing. Ferrous sulfate is used as a mordant, the absolute value of $a^*$ value increases, the $b^*$ value decreases, the green light increases, the yellow light decreases, and the dyeing depth increases. Potassium aluminum sulfate is used as a mordant, the absolute value of $a^*$ value increases, the value of $b^*$ decreases, the green light increases and the yellow light decreases, but the dyeing depth does not change significantly. Copper sulfate is used as a mordant, the absolute value of $a^*$ value increases, the $b^*$ value decreases, the green light increases, the yellow light decreases, the dyeing depth increases and the change is most obvious due to the influence of copper ions. By using different mordants, different blue colors can be dyed.

Compared with direct dyeing, the color fastness of mordant dyeing is improved. This is because the metal ions of the mordant form a complex with the fiber and the gardenia blue pigment, which improves the binding force between the dye and the fiber. The color fastness is improved differently depending on the mordant.

4 Conclusions and prospects
The production process of plant dye is essentially a process of pigment extraction, which will leave a certain amount of residue. These substances are the stage products in the natural circulation system, which can not only decompose naturally, but also be used as high-quality fertilizer after certain treatment. The color of cashmere fiber dyed with plant dyes is elegant, mild and comfortable, which conforms to the application style of raw materials. It can be used to develop high-grade cashmere intimate products, such as underwear and pajamas. It also meets the requirements of environmental protection and ecology, and conforms to the urgent pursuit of modern people for health and ecological life mode. Meanwhile, novel coronavirus pneumonia has been widely focused on the outbreak of the recent outbreak of new crown pneumonia. Most of the dyes have pharmacological effects, and have antibacterial and anti-inflammatory effects. This will enable the plant to dye functional cashmere products with great market competitiveness and development prospects.

Due to the determinable row deviation of plant dyes, the growth of plant dyes is affected by different climate, collection time and origin, and the composition is unstable, resulting in the instability of dyeing color, different hue and saturation. Therefore, the relevant information of the experiment is given: the experimental site is Huzhou, Zhejiang Province; the experimental climate is subtropical monsoon climate from April to June. The optimum dyeing conditions of gardenia blue pigment were as follows: pH of dyeing solution 4, dye mass fraction of 7.5% o.w.f, temperature 75 ℃, time 50 mins, bath ratio 1:30. It can provide some reference for the follow-up researchers to carry out the gardenia blue staining experiment.

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