Study on dyeing of vegetable tanned leather with indigo

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Abstract. In order to improve the dyeing fastness of indigo plant dyes for leather, save the cost of dyeing and reduce the environmental pollution in the dyeing process, the appearance quality is improved by improving the traditional indigo dyeing method. In this study, we try to use indigo acid environment to dye vegetable tanned leather to avoid the damage of basic environment to leather in the process of indigo vat dyeing. The single factor and orthogonal experiments of indigo natural dye dyeing vegetable tanned leather were carried out with the amount of iron medium, indigo dye, dyeing temperature and pre-mordant dyeing time as experimental parameters, and the dyeing effect was evaluated with the K/S levels and color fastness as measurement indexes. The results showed that the concentration of iron powder was 10 g/L, the pre-mordant dyeing time was 25 minutes, the concentration of indigo was 16 g/L, and the dyeing temperature was 35 °C; the vegetable tanned leather after dyeing had better K/S levels, dry wet friction and tensile strength, but the light fastness needs to be further improved.

1 Introduction

According to modern scientific concepts, dyes are organic compounds and other substances that can strongly absorb and transform the light energy of visible light, far ultraviolet light and near infrared light. At present, most of the leather dyes which are widely used are made from petrochemical products, and they will produce many harmful substances in the production process. They will not only pollute the environment in the production process, but also leave carcinogens in the dye products, causing harm to human body. As a representative of green eco dyes, the development and application of natural dyes have become an important direction of leather dyes research. The concept of green leather making puts forward new requirements for leather dyes.

Different plant dyes have different dyeing mechanism, different fiber types and different dyeing texture. At the same time, because of the complex structure of plant dyes, so far, many plant dyes' dyeing mechanism is still under exploration. As protein fibers, wool dyeing research has a certain reference significance for leather dyeing. Zhang Yan [1] research shows that indigo pigment dyeing is close to the traditional VAT indigo dyeing, and the dyeing percentage, levelness and color fastness of wool after dyeing meet the requirements of processing and taking. The structure of edible indigo pigment is similar to that of natural indigo, with two sulfonic groups added, which increases the water solubility of the dye and has no effect on the chromogenic group. Wang Xuemei [2] et al. Studied the dyeing process of walnut green skin pigment in wool fiber. The plant pigment has good solubility in water and good...
levelling effect. Different mordants have certain influence on dyeing. In the field of leather dyeing, Dai Huiju [3] and so on, it has been found that the absorbance at 603nm of indigo at 0-30ug/ml has a good linear relationship, which can accurately analyze the concentration below 30ug/ml. Zheng Shunji [4] found that chitosan quaternary ammonium salt, as a new modified product, has more cations than chitosan. When it adsorbs on the fiber surface, it greatly increases the number of dye sites on the anionic dye and has stronger adsorption on the anionic dye.

In order to be able to dye correctly in the actual production, in addition to understanding the structural characteristics and application performance of various dyes, it is also necessary to understand the properties of dye solution, leather properties and the principle of the function of dyes on leather with different properties. The traditional indigo dyes are insoluble in water and have no affinity for fibers. It is necessary to reduce indigo to soluble cryptochrome by reducing agent in alkaline solution so as to be absorbed by fibers. Leather is rich in protein fibers, acid and alkali resistant. The basic conditions of reducing dyes will cause damage to leather fibers, so natural indigo dyes are not suitable for leather dyeing. Vegetable tanned leather, also known as tannin extract leather, is a kind of leather tanned with vegetable tanning agent. It is a kind of green environmental protection leather that can be directly contacted with skin and is harmless to human body. In this study, indigo pigment was used to dye vegetable tanned leather to explore the feasibility of environmental protection dyeing of vegetable tanned leather and the optimal process index.

2 Experimental part

2.1 materials, equipment and instruments
a) Materials: 1.0 mm primary color vegetable tanned leather, 2.5 * 15cm rectangle, each piece weighs about 2.5g.
   b) Reagent: water soluble natural indigotin, sodium methylene naphthalenesulfonate (dispersant) NNO, all of which are analytical pure, iron medium powder (mordant).
   c) Equipment and instruments:
      JA2003N electronic balance, hh-8 double row eight hole digital display constant temperature water bath pot, pen orp-286 potentiometer, desk pH acidity tester, y571b friction color fastness tester (Nantong Hongda Experimental Instrument Co., Ltd.), bgY9802a-5 standard light source box (Nantong Hongda Experimental Instrument Co., Ltd.), sf300 thinker computer color tester (Thinker Color Technology Co., Ltd.).

2.2 dyeing process design
The mordant dyeing method can make the dye more firmly fixed on the fiber, not only can improve the color fastness of leather, but also can increase the depth of leather dyeing by using different mordants. The dyeing of leather with natural dyes is mostly carried out with metal salts or organic acids as mordants, so that collagen can form a more solid complex structure can obtain better dyeing effect. When metal ions are used to mordant dyeing, metal ions are used as central ions to form coordination reactions with coordination groups on fabrics and dyes respectively. The formation of complexes can make natural dyes better dye protein fibers. Iron ions are located in the eighth group of the fourth period of the periodic table of elements, and they have a strong ability to be coordination formers. In the process of mordant dyeing, the dye molecules adsorbed on the surface of protein fiber form an insoluble complex with metal ions and are fixed on the fiber, which can obviously improve the dyeing fastness of natural dyes. The mordant dyeing method can be divided into three kinds: pre mordant, post mordant and co mordant. In this experiment, the pre mordant, post mordant and co bath are tested first. From the comparison of dyeing effect, the pre mordant dyeing method can improve the dyeing depth more. Therefore, the pre mordant dyeing method is used in this test. The dispersing agent NNO is easy to dissolve in any hardness water, anionic type; the chemical names are sodium methylene naphthalene sulfonate and sodium methylene naphthalene sulfonate, which have excellent diffusivity and protective colloidal properties. The dispersing agent NNO has good diffusivity and protective colloidal properties,
but it has no surface activity such as penetration and foaming, has affinity for protein and polyamide fiber, and has no affinity for cotton, hemp and other fibers. [5]

2.5g skin was dyed in 250ml dye solution with bath ratio of 100:1; In this study, the content of iron powder $X_1$ ($X_1 = 2.4 \text{ g/L}$), indigo content $X_2$ ($X_2 = 4, 8, 12 \text{ g/L}$), dyeing pH $X_3$ ($X_3 = 3, 4, 5, 6, 10$), mordant dyeing time $X_4$ ($X_4 = 25, 30, 35, 40 \text{ min}$), dyeing temperature $X_5$ ($X_5 = 25, 30, 40 ^\circ\text{C}$) as the main experimental factor, single factor experiment was carried out, and the basic process quantity was designed: mordant temperature of iron powder $X_1$ was $25 ^\circ\text{C}$, dispersant NNO (0.025g), dyeing time was 60min, during which the potential and pH value were measured for 4 times, and then washed and dried after dyeing. Process flow and single factor variable range are shown in the figure.

2.3 Experimental method

2.3.1 Single factor experiment. Single factor experimental design refers to the experiment with only one research factor, that is, researchers only analyze the effect of one factor on the effect index. One of the main objectives of this experimental design is how to control the influence of confounding factors on the research results. In this study, five groups of factors, i.e. iron content, mordant dyeing time, indigo content, dyeing temperature and dyeing pH, were taken as experimental samples to dye 32 vegetable tanned leather samples. The dyeing effect was evaluated by K/S levels. [6]

2.3.2 Orthogonal experiment design. Five process parameters, i.e. iron powder concentration, indigo dye dosage, dyeing pH value, dyeing temperature and pre mordant dyeing time, are selected as orthogonal test factors. Each factor is designed as 4 levels. Each level value determined according to single factor test results is shown in Table 1.

| level | Dyeing pH | Indigo (g/L) | Dyeing temperature | Mordant time (min) | Iron coal powder (g/L) |
|-------|-----------|--------------|---------------------|--------------------|-----------------------|
| 1     | 5.5       | 2            | 25                  | 25                 | 1.5                   |
| 2     | 6.0       | 3            | 30                  | 30                 | 2                     |
| 3     | 6.5       | 4            | 35                  | 35                 | 2.5                   |
| 4     | 7         | 5            | 40                  | 40                 | 3                     |

2.3.3 Color fastness to dry and wet rubbing, sunlight fastness and tensile test. According to the national standard GB/T22885-2008 leather color fastness test standard, the dry and wet rubbing color fastness of the optimal dyeing scheme was measured; According to QB / T8427-2019 leather color fastness test, the light fastness was tested; and the tensile test was carried out for the non dyed vegetable tanned leather, indigo dyed leather and reduced indigo dyed leather.

3 Results and analysis
3.1 Single factor experiment

3.1.1 Effect of dyeing pH on K/S levels. In the process of indigo pigmented leather dyeing, in addition to temperature, time, dosage of chemicals and so on, the pH can control the acid ions in the dye solution, and the strength of the ion bond can be changed due to the pH, so the acid value is properly controlled. The more the vegetable tanned leather fiber and the dye are combined, the stronger and the easier to color, the higher the relative rate of color application, and the less the dye residue.

The pH value of strong acid dye is 2-4, weak acid dye is 4-6, and neutral dye is 6-7. In this experiment, as shown in Figure 2, the best state of dyeing K/S levels is pH 6. In the dyeing process, the acid used to adjust the pH is acetic acid. Before use, dilute it with distilled water, and drop acetic acid diluent into the rubber head dropper. After adding acetic acid, the pH of dyeing solution is maintained in weak acid condition, leather has negative charge, and dye also has negative charge. Under the joint action of van der Waals force, hydrogen bond and ion bond, it is conducive to the wetting, expansion and diffusion of leather fiber, and plays a leveling role.

![Figure 2](image1)

**Figure 2.** The influence of dyeing pH on K/S levels

3.1.2 Effect of indigo content on K/S levels value. As shown in the figure, when the indigo content reaches 3g, K/S levels peak will appear. When the indigo content is higher than 3g, K/S levels will not be improved. This result shows that when the indigo content reaches a certain saturation, the dyeing reaction will be complete, and the dyeing process will not be enhanced with the increase of indigo content. In the orthogonal experiment, the value may be in the range of 3-4g with the dynamic change of the factors in the process curve.

![Figure 3](image2)

**Figure 3.** Effect of indigo content on K/S levels value

3.1.3 Iron pulverized coal content. Iron is used as a mordant to coordinate with the negative dye ions. The coordination bond is formed by electrostatic attraction to coordinate with the negative dye anions. The coordination bond is formed by electrostatic attraction to form a stable complex between the dye metal iron leather, so as to improve the dye uptake and dyeing fastness. In this single factor experiment, K/S levels of 6 samples were obtained from the content of 0.5-3 g / L iron powder. As shown in the figure, when the content of iron pulverized coal is 2.5g/l, K/S levels reaches the maximum value. As a
reference, the content of iron pulverized coal in the orthogonal experiment is 1.5, 2, 2.5 and 3g/L as the grade difference.\[^9\]

**Figure 4.** Effect of iron pulverized coal content on K/S levels

3.2 Analysis of orthogonal experiment results

Dyeing pH > indigo content > mordant dyeing time > iron powder content > dyeing temperature. The optimum process parameters of indigo natural dye for vegetable tanned leather dyeing are A1B3C2D1E3, that is, the pH of dyeing is 5.5, the concentration of indigo dye is 4g/L, the dyeing temperature is 30\(^\circ\)C, the pre mordant dyeing time is 25 minutes, and the concentration of iron powder is 2.5g/L.\[^9\]

| orthogonal | dyeing pH A (weak acid) | indigo B (g/L) | Dyeing temperature C(\(^\circ\)C) | Media time D (min) | Iron powder E (g/L) | K/S levels |
|------------|-------------------------|----------------|-------------------------------|-------------------|---------------------|------------|
| 1          | 5.5                     | 2              | 25                            | 25                | 1.5                 | 6.7809     |
| 2          | 5.5                     | 3              | 30                            | 30                | 2                   | 6.7851     |
| 3          | 5.5                     | 4              | 35                            | 35                | 2.5                 | 7.3685     |
| 4          | 5.5                     | 6              | 40                            | 40                | 3                   | 8.2209     |
| 5          | 6                       | 6              | 30                            | 35                | 3                   | 5.5791     |
| 6          | 6                       | 2              | 25                            | 40                | 2.5                 | 6.3580     |
| 7          | 6                       | 3              | 40                            | 25                | 2                   | 6.9302     |
| 8          | 6                       | 4              | 35                            | 30                | 1.5                 | 7.2713     |
| 9          | 6.5                     | 6              | 35                            | 40                | 2                   | 5.257      |
| 10         | 6.5                     | 2              | 40                            | 35                | 1.5                 | 5.339      |
| 11         | 6.5                     | 3              | 25                            | 30                | 3                   | 6.328      |
| 12         | 6.5                     | 4              | 30                            | 25                | 2.5                 | 8.394      |
| 13         | 7                       | 6              | 40                            | 30                | 2.5                 | 5.809      |
| 14         | 7                       | 2              | 35                            | 25                | 3                   | 5.203      |
| 15         | 7                       | 3              | 25                            | 40                | 1.5                 | 6.410      |
| 16         | 7                       | 4              | 30                            | 35                | 2                   | 6.037      |
| K1         | 7.288                   | 5.920          | 6.469                         | 6.827             | 6.450               |
| K2         | 6.534                   | 6.613          | 6.698                         | 6.548             | 6.252               |
| K3         | 6.329                   | 7.267          | 6.281                         | 6.081             | 6.982               |
3.3 Test results of color fastness to dry and wet rubbing, sunlight fastness and tensile strength
The color fastness of dry and wet rubbing is grade 4 and grade 3 respectively, but, Color fastness to sunlight only reaches level 2. The maximum tensile stress of vegetable tanned leather is 7.964 mpa, which can be improved by acid indigo dyeing. The maximum tensile stress is 9.113 MPa.

| Rubbing fastness / grade | Fastness to sunlight / level | Maximum tensile stress (MPa) |
|-------------------------|-----------------------------|-----------------------------|
| Dry friction, wet friction | Colorfastness to light | Unstained, acid stained, reduced indigo stained |
| K4                     | 5.865                      | 6.216  | 6.575  | 6.561  | 6.332  |
| R                      | 1.42                       | 1.35   | 0.42   | 0.75   | 0.73   |

4 Conclusion
4.1 The maximum tensile stress of vegetable tanned leather is 7.964 mpa, which can be improved by acid indigo dyeing. The maximum tensile stress is 9.113 MPa.

4.2 When vegetable tanned leather is dyed in acid condition, the best dyeing conditions are as follows: iron powder concentration of 10 g / L, pre mordant dyeing time of 25 minutes, indigo concentration of 16 g / L, dyeing temperature of 35℃.

4.3 Indigo vegetable tanned leather has better dyeing fastness under the best dyeing conditions, but the fastness to sunlight is not good.

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