Extraction and Dyeing Propertie of Tannin from Walnut Green Husk

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Abstract. Ultrasonic method for the extraction of tannin from walnut green husk was performed. In order to measure the content of tannin, folin-ciocalteu method was employed in this paper. Ultrasonic time, solvent concentration, temperature were selected for the single-factor experiment. By orthogonal experiment , the optimum condition was determined as acetone concentration was 50%, extracting temperature was 55°C, extracting time was 3.5h. In this condition, the actual content of tannin could reach to 27.37mg/g. In this paper, the crude extracts of tannin from walnut green husk was used to dye something. The results had shown that when ferrisulphas was used to as a mordant, the coloring degree would be the deepest. The coloring degree became deeper and deeper with the dyeing time increasing. There was no significant difference in coloring degree between 80 min and 100 min.

1. Introduction

In Chinese folk, the green walnut wine had been used to treat the pain of dysmenorrhead and cancer instead of morphine, opium tincture as well as other pain relievers, and good analgesic effects had been received. Extracts from walnut green husk had good bacteriostatic activities[1]. Some researchers[2-6] had demonstrated that walnut green husk contained a great variety of antioxidant components. Walnut green husk could be developed in many ways, it could be made into walnut green biochar[7]. At present, the chemical constituents of walnut green husk were mostly focused on the antioxygenation of polysaccharide[8-9], anthraquinones as colouring material[10-11], extracting technology of flavonoids[12-13] and antibacterial activities as well as the action of antitumor of juglone[14-15], there were few studies on tannin, but the content of tannin was second only to flavone and anthraquinones in walnut green husk [16]. So it was necessary to study the tannins from walnut green husk in order to use it as colorant.

The structure of tannin was complex and it was difficult to synthetize . At present, it was mainly extracted from natural plants at home and abroad, it was economic significance that we extracted

tannin from walnut green husk. In china, there were some problems in natural dyes, such as lacking of raw materials, low color fastness and poor stability. At the same time, due to its low extracting rate and low purity, it was difficult to produce on a large scale, and large scale production led to the occupation of cultivated land or damaged to it, which was not consistent with China national conditions and didn't adapt to the national environmental protection policy [17]. In this paper, the extracts of walnut green husk could be used as natural colorant.

2. Materials and Reagent

2.1 Materials

The walnuts were harvested from luancheng district, shijiazhuang city, hebei province in 2017.

2.2 Reagents

Acetone was purchased from Beijing Chemical Works, China. Tannic acid was purchased from Tianjin Kermel Chemical Reagent Development Center, China. Acetone and tannic acid were of analytical grade.

3. Experimental Methods

3.1 Preparation of Standard Solution

The 1.0mg tannin sample was placed in a 100mL brown flask, dissolved in water, diluted to scale and shook well, then got the standard solution.

3.2 Linear Relation Survey

The sample of the 0, 2.0, 4.0, 6.0, 8.0 mL was respectively mixed with 0.5mL folin-ciocalteu and them were added into 10mL brown bottle, shook well, remained stationary for 6min. Then 1mL 20% Na_2CO_3 solution was added in the brown bottle, added distilled water to scale, measured the light absorption value at wavelength 760 nm. The standard curve was drawn with the mass concentration of tannic acid c(mg/mL) and the absorbance value A [18-19].

3.3 Single-Factor Experiment

Concentration of acetone, ultrasonic temperature and ultrasonic time on the extraction of tannin from walnut green husk were assessed.

The 10.0g walnut green husk were cut into pieces 1cm×1cm; extractions were performed at different concentration of acetone (30%, 40%, 50%, 60% and 70%) and at different ultrasonic temperature (40℃, 50℃,60℃, 70℃, 80℃), ultrasonic time (1.5, 2, 2.5, 3, 3.5h), and the solvent to sample ratio (30:1). The suspensions were then filtered by filters; filtered through a rotary evaporator at 50℃; dissolved by 40mL distilled water; filtered to remove insoluble matter; metered volume to 50 mL with distilled water; diluted 10 times; the 1 mL extracting solution was developed according to the optimal experiment; and then measured the light absorption value three times at wavelength 760 nm; then, the light absorption value was taken into the standard curve to calculate the content of tannin.

3.4 Orthogonal Design

The 10.0g walnut green husk was added in 9 conical flasks respectively, the extracting rate of tannin was taken as the index, and the temperature, solvent concentration and ultrasonic time was selected as the factors, The experiment was carried out according to $L_9(3^4)$ orthogonal table to investigate the extracting technology of tannin from walnut green husk. Each factor was set at 3 levels, as shown in table 1.

Table1. Orthogonal Experimental Factors of Extracting Technology of Tannin from Walnut Green Husk.

Levels	A Time/h	B Solvent Concentration/%	C Temperature/℃
1	2.5	45	45
2	3	50	50
3	3.5	55	55

3.5 Preliminary Study on Dyeing Effects

This paper focused on the influence of different metal ions and different time on dyeing effects to provide a reference for developing new dyeing products.

3.5.1 Preparation of Hair Dyes and Influence of Different Dyeing Time on Dyeing Effects

Ultrasonic extraction was carried out according to the best extracting technology of crude extracts of tannin, we could obtain the crude powder over filtered, the evaporated was at 50℃, vacumm drying was at 50℃. 5g powder was dissolved in 50mL distilled water, and then
hair dyes could be obtained by adding respectively 1.5g of ferrisulphas, magnesium acetate, sodium sulfate, copper sulfate, potassium chloride.

7.5g grey dog's hair was divided into 5 parts on average, then they were added in the dyeing liquid, and were performed at 40℃ for 1h.

3.5.2 Influence of Different Dyeing Time on Dyeing Effects

25g powder of walnut green husk with 7.5g ferrisulphas were added in 250mL distilled water, and it was divided into 5 parts on average, and then, they were performed at 40℃and at different time (20, 40, 60, 80, 100 min).

4. Results and Discussion

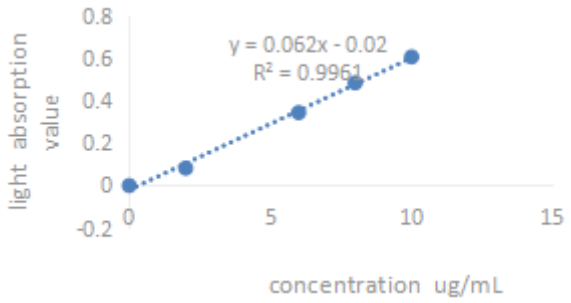

Figure 1. Standard Curve of Tannic Acid.

As shown in figure 1, the regression equation: Y =0.062X-0.02 (r = 0. 9961), it showed that tannic acid had a good linear relationship between 0 and 10.00 μg·mL^{-1}.

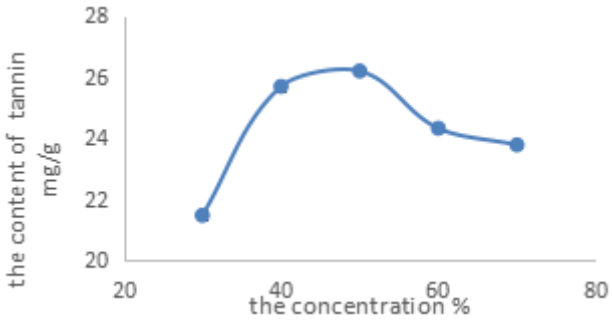

Figure 2. Effects of Different Concentrations of Acetone on Tannin.

It could be seen from figure 2 that with the increasing of concentration of acetone, the extracting amount of tannin would increase firstly, when the concentration of acetone reached to 50%, the extracting amount reached to the highest level, however, when the concentration exceeded 50%, the extracting amount of tannin decreased gradually, with the increase of the concentration of acetone, the dissolution of other substances would hinder the extraction of tannin.

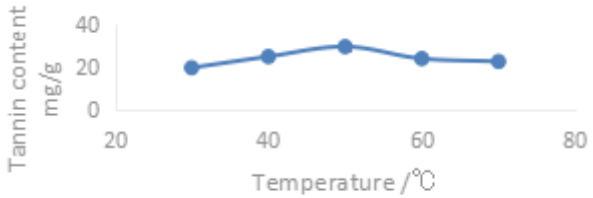

Figure 3. Effects of Different Temperature on Tannin.

We could learn from figure 3 that with the rise of temperature, the amount of tannin extracting would increase firstly, however, when the temperature exceeded 50℃, the extracting amount of tannin decreased gradually. It might because high temperature affected the stability of tannins.

Figure 4. Effects of Different Time on Tannin.

According to figure 4, we could conclude that with the extension of ultrasonic time, the amount of tannin extracting would increase firstly, when the ultrasonic time exceeded 3.0h , the extracting amount of tannin decreased gradually. It was the long time of ultrasonic treatment led to the high temperature, which affected the stability of tannin.

Table 2. Orthogonal Experimental Results of Extracting Technology of Tannin from Walnut Green Husk.

No.	A	B	C	The content of tannin mg/g

1	1	1	1	20.8401
2	1	2	3	23.886
3	1	3	2	21.0137
4	2	1	2	20.0137
5	2	2	3	23.9045
6	2	3	1	19.6425
7	3	1	3	25.6848
8	3	2	2	23.0533
9	3	3	1	22.5456
K1	65.7398	66.5386	63.0258	
K2	63.5607	70.8438	64.0807	
K3	71.2837	63.2018	73.4753	
k1	21.9133	22.1795	21.0094	
k2	21.1869	23.6146	21.3602	
k3	23.7612	21.0673	24.4918	
R	2.5743	2.5473	3.4824	

Table 3. Analysis of Variance of Extracting Technology.

Source	SS	df	F	P
Time	10.585	2	23.698	＜0.05
Solvent Concentration	0.185	2	0.414	＞0.05
Temperature	12.421	2	27.808	＜0.05
Error	0.447	2		

It could be seen from table 2 and table 3 that the order of influence of each factor on the extracting technology was C>A>B, temperature had great influence, followed by extracting time. Analysis of variance showed that factors A and C had significant effects on extracting technology. We could determine that the optimal combination was A3B2C3, the results showed that extractions were performed at 50% acetone, 55℃, 3.5h. Three validation experiments were carried out according to the optimal technology, and the results showed that extracting amounts of tannin were 27.48, 26.62 and 28.01 mg/g, the optimal extracting technology was stable.

Table 4. Dyeing Effects of Different Metal Ions.

Different Metal Ions	Different Colours
ferrisulphas	Brown
magnesium acetate	Brown
sodium sulfate	Sandy Beige
copper sulfate	Grey
potassium chloride	Yellow

Table 5. Influence of Different Metal Ions on Dyeing Effects.

Different Metal Ions	L*	a*	b*	ΔE
standard sample	47.36	2.03	6.23	

ferrisulphas	35.16	4.38	8.89	12.71
magnesium acetate	35.90	4.76	8.78	12.05
sodium sulfate	39.95	6.24	12.05	10.32
copper sulfate	35.62	3.10	6.56	11.82
potassium chloride	39.09	5.81	12.00	10.77

It could be seen from table 4 and table 5 that ferrous ion, magnesian ion were mordants with good dyeing effect.

Table 6. Influence of Different Dyeing Time on Dyeing Effects.

Time	L*	a*	b*	ΔE
standard sample	47.36	2.03	6.23	
20 min	42.24	3.70	6.93	5.43
40 min	40.00	5.11	10.06	8.85
60 min	39.51	6.36	13.43	11.50
80 min	36.68	5.94	12.97	13.22
100 min	35.93	6.42	11.46	13.31

It could be seen from table 6, the staining lasted from 80 to 100 min, and there was no difference between 80 to 100 min. So in order to save time, we cuold selecte for 80min.

5. conclusion

The tannins contained in walnut green husk are hydrolyzed tannins[20-21], therefore, this paper used folin-ciocalteu method[22] to determine tannin of walnut green husk, this method was simple and rapid and showed satisfactory selectivity and repeatability. We determined the best extracting technology of tannin from walnut green husk: extractions were performed at 55℃ for 3.5h, extracting solvent was 50% acetone. In this condition, the maximum amount of tannin could reach to 28.01 mg/g, it showed that walnut green husk had good development value. Ferrous ion was found to have better dyeing effect through the study of dyeing effect. It could also be used for dyeing cotton fabric, providing more ways for comprehensive utilization of walnut green husk.

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