Development of citrus peel ethanolic extract shampoo

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Abstract. The citrus peel ethanolic extract shampoo was prepared via adding the ethanolic extract, soxhlet extracted from citrus peel into the shampoo matrix through an orthogonal experiment. Meanwhile, the foam height was determined by heat and cold stability test. The experimental results show that the citrus peel ethanolic extract in a ratio of 8.0% creates a favourable compatibility by the surface agent. There was no delamination after the samples have a heat and cold stability test for 24 h.

1. Introduction

At present, China produces over 10 million tons of citrus peel (Citrus reticulata Blanco) pomace annually [1]. Except for a few feed and proprietary Chinese medicinal formulations, approximately 99% of citrus peels are discarded. Ethanolic extracts, pectin, and other similar substances from discarded citrus peels can improve resource utilization, increase economic benefits, and reduce environmental pollution.

The extraction of ethanolic extract is one of the most important ways to use citrus peel rationally. The ethanolic extract is a mixture containing limonene as the main component, as well as geraniol, terpineol, citral, and caryophyllene [2]. The citrus peel is rich in many nutrients, such as vitamin C, carotene, and protein. The shampoo can infuse hair growth with necessary nutrients, refine damaged hair, and enhance the toughness of hair. Moreover, it can promote blood circulation in the skin, induce metabolism, nourish the scalp, and induce hair growth in a good environment.

Shampoos with plant extracts as active ingredients are not as popular mainly because the traditional extraction process of citrus peel ethanolic extracts is complicated. Moreover, the extraction circle is long; and active ingredients are hard to be extracted [3]. Simplifying the extraction and increasing extraction efficiency of the active ingredients are important. Furthermore, industrial preparation of traditional shampoo has been developed and its experimental operation is relatively simple. Shampoo preparation has been reported in various literatures locally and globally [3-5]. In this study, we first combined citrus ethanolic extract with shampoo in order to prepare a novel citrus peel ethanolic extract shampoo.
2. Experimental

2.1. Chemical reagent
Polyoxyethylene lauryl ether sodium sulfate (98%, Jiaxing sicheng chemical Co. Ltd), coconut oil diethanolamide (98%, Bide Pharmatech Ltd), sodium dodecylbenzene sulfonate (30%, Sinopharm chemical reagent Co. Ltd), lauryl dimethyl betaine (30%, Bide Pharmatech Ltd), sodium chloride (99.5%, Sinopharm chemical reagent Co. Ltd), citric acid (99.5%, Sinopharm chemical reagent Co. Ltd), sodium benzoate (99.5%, Jiaxing sicheng chemical Co. Ltd), polyquaternium-39 (> 99%, Jiangsu beida medical technology o. Ltd), guar gum (99%, Guangzhou liaohua chemical Co. Ltd), Methyl 4-hydroxybenzoate (≥ 98%, Shanghai Excellent Chemical Co. Ltd), kathon (≥ 95%, Shandong Jiayu Chemical Co. Ltd), peptone (>95%, Xiamen yiweilong biotechnology Co. Ltd), beef extract (biological reagent, Shanghai bio-engineering Co. Ltd), anhydrous ethanol (99.9%, Sinopharm chemical reagent Co. Ltd). Water for preparation of and reagent solutions was produced in-house by the Milli-Q water purification system (Millipore, Milford, MA, USA).

Ethanolic extract, which was peeled immediately to extract the active ingredient by soxhlet extractor from the citrus peel.

2.2. Instrument
The instruments as follows: model 2152 Roche foam instrument (Shanghai Longtop Instrument Equipment Co. Ltd), SPX-250B-Z biochemical incubator (Shanghai Boson Industrial Co. Ltd), DHG-9240A digital display blast oven (Shanghai Qixin Scientific Instrument Co. Ltd), DF-101S heat collecting magnetic stirrer (Henan Gongyi Yihua Instrument Co. Ltd), YXQ-LS-70A vertical pressure steam sterilizer (Shanghai Boson Industrial Co. Ltd), DW-25W300 cryogenic refrigerator (Qingdao Haier Special Electrical Appliances Limited), and NAI-CCQ-150S Soxhlet extractor (Shanghai Qiqian Electronic Technology Co. Ltd), VISCO Portable digital display viscometer (Changchun Leyi Technology Co. Ltd.).

2.3. Shampoo preparation
The steps for preparing shampoo are as follows: 1) measure the deionized water and pour it into a beaker, place the beaker in a water bath of magnetic stirrer, and heat it to 60 °C; 2) add the main surfactant and stir until it is completely dissolved; 3) add the co-surfactant below 60 °C to 65 °C and continue to stir until it is completely dissolved; 4) and reduce the temperature to 40 °C, measure the pH value, adjust the pH value with citric acid to 5.5-7.0; and 5) add thickener to adjust its viscosity when the temperature closes to room temperature.

2.4. Sample testing
(1) Heat stability test [6, 7]
Samples are poured into a Ø20 mm × 120 mm test tube. When the liquid level is approximately 80 mm, a clean plug is inserted. A test tube is placed in a constant temperature incubator preadjusted to 40 °C. After 24 h, the test tube is taken out. After the temperature reverts to room temperature, a visual comparison with that in another test tube is performed.

(2) Cold stability test [6, 7]
Samples are poured into a Ø20 mm × 120 mm test tube. When the liquid level is approximately 80 mm, a clean plug is inserted. A test tube is placed in a constant temperature incubator preadjusted to -8 °C. After 24 h, the test tube is taken out. After the temperature reverts to room temperature, a visual comparison with that in another test tube is performed.

(3) Foam height test [6, 7]
A total of 1500 mg/kg hard water is prepared. A total of 3.7 g anhydrous magnesium sulfate and 5.0 g anhydrous calcium chloride are weighed and dissolved in 5000 mL of distilled water fully.

A magnetic stirrer is used to heat the water to 40 ± 1 °C. A hose is used to connect a small water pump to the Roche foam meter. Small water pump is opened to pump the thermostatic water to the
Roche foam meter wall to make the water in the wall and in the water bath circulate. Roche foam meter is kept at a constant temperature of 40 ± 1 °C. A total of 2.5 g sample are weighed, and 900 mL of distilled water is added to dissolve the sample. A total of 100 mL of 1500 mg/kg hard water are added, and water was heated to 40 ± 1 °C. The solution is stirred to dissolve the sample evenly. A 200 mL quantitation funnel is used to take a part of the sample solution and rinse it along the wall of the foam tube. Then, the test solution is placed into the bottom of the foam meter and aligned to the mark at 50 mL. Then, a 200 mL dosing funnel is used to take the test solution, fix the center of the funnel, release the test solution, immediately record the foam height, and record the foam height every 5 min (5 times in total). Repeat the above-mentioned processes, take the average value of the two errors within the allowable range as the final result, and retain the result to the integer number.

(4) Determination of viscosity [5, 6]

The probe of the portable digital viscometer inserted into shampoo sample that was cooled naturally to 25 ℃, and read directly.

(5) Determination of the total number of bacteria, fecal coliform, P. aeruginosa, and S. aureus [6, 7]

The coated medium is placed in an incubator at 37.8 °C for 24 h to 48 h. After 24 h, fecal E. coli, S. aureus, and P. aeruginosa are observed in the corresponding media. However, in the medium, in terms of the total number of bacteria, 48 bacteria are found in the 10-fold dilution, while 8 bacteria are found in the 100-fold dilution.

3. Results and discussion

3.1. Determination of the matrix formula of shampoo

The number represented formula of shampoo, such as ①, ② and ③ etc. the main surfactants, which are the major constituent in shampoo. Meanwhile, corresponding to co-surfactants is the minor ingredient in shampoo.

Table 1 shows that polyoxyethylene lauryl ether sodium sulfate, sodium dodecylbenzenesulfonate (LAS-Na, 30%), and dodecyl dimethyl betaine are the main surfactants.

3.2. Extraction, emulsification, and result analysis of citrus peel ethanolic extract

A total of 30 g fresh citrus peel are sheared into 0.3 cm square pieces, and shredded citrus peels are wrapped in a degreasing filter paper bag and then placed in an extraction tube. Ethanol is placed in an extraction bottle, and the extraction bottle is heated until ethanol vaporizes. Vaporized ethanol rises from the connection tube and condenses into liquid. The liquid is dripped into the extraction tube, and ethanolic extract is extracted from the citrus peel. When the ethanol level in the extraction tube reaches a certain height, ethanol with crude ethanolic extract flows into the extraction bottle through the siphon tube. Heating is continued, and ethanol that has flowed is vaporized and condensed into the extraction bottle and then dropped into the extraction tube. Repeat the processes until extraction is completed.

A total of 2 g citrus peel ethanolic extract are weighed with polyoxyethylene lauryl ether sodium sulfate and dodecyl dimethyl betaine and then heated and stirred rapidly to form an emulsion. Then, surfactant and deionized water was added. The resulting solution is mixed with Formulas ①, ②, ③, ④, ⑤, ⑥, ⑦, and ⑧ to carry out hot and cold tests. Formulas ⑥, ⑦, and ⑧ are stratified. Therefore, the selected formulas of the emulsified base experiment are Formulas ⑤ and ⑥.

Table 2 shows that shampoos prepared with polyoxyethylene lauryl ether sodium sulfate as the main surfactant have good effects on the indicators, and those with sodium dodecylbenzenesulfonate (LAS-Na, 30%) as the main surfactant because of less viscous than the others. Shampoo with dodecyl dimethyl betaine as the main surfactant, together with polyoxyethylene lauryl ether sodium sulfate, sodium dodecylbenzenesulfonate (LAS-Na, 30%), and dodecyl dimethyl betaine, which have good viscosity and cold/heat stability.
Table 1. Design of shampoo surfactant formula.

| Number | Polyoxyethylene laurel ether sodium sulfate | Coconut diethanol amide | Sodium dodecylbenzene sulfonate | Dodecyl dimethyl betaine | Sodium chloride | Sodium citrate | Sodium benzoate | Deionized water |
|--------|--------------------------------------------|-------------------------|---------------------------------|--------------------------|----------------|---------------|----------------|-----------------|
| ①      | 20                                         | 4.0                     | 0                               | 0                        | 2.0            | 0.3           | 0              | Balanced        |
| ②      | 12                                         | 4.0                     | 0                               | 4                        | 0              | 0.3           | 0              | Balanced        |
| ③      | 10                                         | 4.0                     | 5                               | 6                        | 0              | 0.5           | 0.1            | Balanced        |
| ④      | 5                                          | 5.0                     | 15                              | 0                        | 0              | 0.5           | 0.2            | Balanced        |
| ⑤      | 6                                          | 3.0                     | 12                              | 0                        | 0              | 0.7           | 0.2            | Balanced        |
| ⑥      | 20                                         | 2.5                     | 0                               | 0                        | 1.5            | 0.3           | 0.2            | Balanced        |
| ⑦      | 9                                          | 3.0                     | 5                               | 4                        | 2.0            | 0.5           | 0.1            | Balanced        |
| ⑧      | 6                                          | 4.0                     | 0                               | 10                       | 2.0            | 0.5           | 0.2            | Balanced        |

*Balanced, which was kept the shampoo total volume relatively constant.

Table 2. Test results of viscosity, heat stability, and cold stability of shampoo.

| Test indices | ① | ② | ③ | ④ | ⑤ | ⑥ | ⑦ | ⑧ |
|--------------|----|----|----|----|----|----|----|----|
| Viscosity (mpa·s) | 8525.1 | 8965.1 | 9023.1 | 6554.6 | 7525.8 | 7688.5 | 4389.5 | 4965.3 |
| Heat stability | No delamination | No delamination | No delamination | No delamination | No delamination | No delamination | No delamination | No delamination |
| Cold stability | No delamination | No delamination | Delamination | No delamination | No delamination | No delamination | Delamination | Delamination |

*All shampoos’ viscosities meet national standards, which between 7000 and 8000 mpa·s·ws up to the enterprise standard

3.3. Screening of citrus peel ethanolic extract
Formulas screened by orthogonal experiments with 2%, 4%, 6%, 8%, and 10% citrus peel ethanolic extract are emulsified based on the method described above, and then heat/cold stability and foam height are tested. The results are shown in Table 3.
Table 3. Screening results of citrus peel ethanolic extract in the formula of citrus peel ethanolic extract shampoo.

| Citrus peel ethanolic extract/g | Foam height/mm | Heat stability  | Cold stability |
|---------------------------------|---------------|----------------|---------------|
| 2                               | 176           | No delamination | No delamination |
| 4                               | 168           | No delamination | No delamination |
| 6                               | 163           | No delamination | No delamination |
| 8                               | 159           | No delamination | No delamination |
| 10                              | 155           | Delamination    | Delamination   |

Table 3 shows that citrus peel ethanolic extract is added to the shampoo formula at ratios of 2%, 4%, 6%, 8%, and 10%, and it has good compatibility with the surfactant. When the ratio is 10%, shampoo will be delaminated; as the amount of citrus peel ethanolic extract increases, the foam height decreases slightly. However, the height of the foam does not have a significant effect. Generally, when the citrus peel ethanolic extract ratio is 8%, the shampoo has the optimum effect.

3.4. Selection of auxiliary surfactant

3.4.1. Selection of conditioning agent. Polyquaternium-39 is salt ion cellulose with excellent antistatic, conditioning, foam-stabilizing, and thickening effects and will not be deposited. Furthermore, polyquaternium-39 can reduce the irritation of detergents on skin. Cationic guar gum has good antistatic and conditioning effects and can improve hair combing, foam rising, and foam stabilization.

3.4.2. Selection of preservatives. The preservatives currently used include Methyl 4-hydroxybenzoate, sodium benzoate, and kathon. Methyl 4-hydroxybenzoate exists in shampoo in the form of micelles, which can reduce the chance of entering bacterial cells and does not inhibit the growth of Staphylococcus aureus and Pseudomonas aeruginosa. Methyl 4-hydroxybenzoate has a relatively poor preservative effect. Sodium benzoate is available in alkaline environments. Kathon can inhibit the growth of bacteria and fungi and has a wide pH range. Therefore, Kathon can be used as a preservative.

3.5. Sample performance

3.5.1. Physical and chemical performance tests. Heat stability test, put the shampoos in an oven for 24h at 40°C. After it returned to room temperature, observed whether discoloration, precipitation, or separation occurred, the indicator was up to GB/T 29679-2013 [7].

Cold stability test, the shampoo was put in a refrigerator for 24 h at -5°C, observed whether discoloration, precipitation, or separation occurred after it returned to room temperature, the indicator was up to GB/T 29679-2013 [7].

3.5.2. Determination of the total number of bacteria, fecal coliform, P. aeruginosa, and S. aureus. No bacteria are found in the 1000- and 10000-fold dilutions, that is, the total number of bacteria is 480 CFU/g. No mold and yeast are observed in the potato culture medium 48 h later. This result agrees with the National Cosmetic Hygiene Standard. Detailed information is shown in Table 4.
Table 4. Indicators of the sensory and sanitary tests of the shampoo.

| Items          | Indicators                  | QB/T 1974-2004 | Measured indicators | Evaluation |
|----------------|-----------------------------|-----------------|---------------------|------------|
| Hygiene indicators | Total number of colonies    | ≤1000           | <10                 | Qualified  |
|                | Fecal coliform              | Not detected    | Not detected        | Qualified  |
|                | Pseudomonas aeruginosa      | Not detected    | Not detected        | Qualified  |
|                | Staphylococcus aureus       | Not detected    | Not detected        | Qualified  |

4. Conclusions

(1) Polyoxyethylene lauryl ether sodium sulfate, sodium dodecylbenzenesulfonate and dodecyl dimethyl betaine are selected as the compositions of the matrix formulation of citrus peel ethanolic extract shampoo.

(2) Considering that the addition of citrus peel ethanolic extracts will affect the stability of the shampoo’s compounding system, such as delamination, viscosity, discoloration, hygiene, and even the quality of the product, the added amount of citrus peel ethanolic extract should be 8%. The experimental results show that the citrus peel ethanolic extract in a ratio of 8.0% creates a favorable compatibility by the surface agent. There was not go bad when layering after the samples have a heat and cold stability test for 24 h. and the performance indicators were agreement with QB/T 1974-2004

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