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Purification of Total Flavonoids from Angelica Dahurica by Macroporous Resin Coupled with UiO-66-NH_2 and Prospect of Residue 3D Printing Recycling

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Abstract: Aiming at the problems of herb residue waste, abundant impurities in crude extracts and poor selectivity of traditional purification methods in the traditional Chinese medicine extraction industry, this study established a two-step purification process combining preliminary separation by macroporous resin and deep refining with UiO-66-NH_2 for total flavonoids from Angelica dahurica. Total flavonoids were extracted via ultrasound-assisted extraction with 70% ethanol, and the content was quantified by rutin colorimetry. Five types of macroporous resins were screened to prepare crude flavonoid sample Group A. UiO-66-NH_2 was synthesized by solvothermal method and characterized by FT-IR and SEM to investigate its adsorption selectivity, adsorption kinetics and cyclic stability. High-purity flavonoid sample Group B was obtained after secondary refining. The results showed that the two-step purification effectively improved the purity of the product. The refined sample exhibited stronger antioxidant activity and tyrosinase inhibitory activity with stable moisture absorption and retention performance, which can be applied as cosmetic raw materials. The two-step purification process developed in this study provides a reference for the pharmaceutical development of high-purity Angelica dahurica flavonoids, and offers ideas for further research on resource utilization of herb residues.

Keywords: solid waste resource utilization; UiO-66-NH_2; total flavonoids from Angelica dahurica

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1. Introduction

In the industrial production of traditional Chinese medicine extraction, improper disposal of herb residues leads to biomass waste and environmental pressure, making green refining and resource recycling of active ingredients an important development trend in this field[1]. Total flavonoids from Angelica dahurica possess excellent antioxidant and whitening activities, showing great potential in the development of medicinal skin care raw materials. Nevertheless, the ethanolic crude extract of Angelica dahurica contains massive macromolecular impurities such as pectin and protein, which easily block adsorbents, reduce purification efficiency and result in substandard product purity[2]. Conventional macroporous resins rely on non-specific physical adsorption based on polarity difference, failing to remove trace impurities with similar

polarity, thus limiting purification depth and failing to meet the preparation standard of pharmaceutical-grade high-purity flavonoids. To solve these drawbacks, amino-modified MOF material UiO-66-NH_2 was fabricated in this work, and a two-step purification system consisting of preliminary separation by macroporous resin and deep refining by UiO-66-NH_2 was constructed. The purification efficiency, interaction mechanism and variation rule of product bioactivity were systematically explored. The adaptability to pharmaceutical development and green application potential of this process were evaluated, providing theoretical and experimental support for the green preparation and pharmaceutical research of high-purity total flavonoids from Angelica dahurica.

2. Materials and Methods

2.1. Raw Materials and Instruments

Raw materials included Angelica dahurica medicinal herb and rutin reference substance. Analytical-grade reagents contained anhydrous ethanol, sodium nitrite, aluminum nitrate, sodium hydroxide, etc. Five commercially available macroporous adsorption resins with different polarities were adopted. Raw materials for synthesizing UiO-66-NH_2 included zirconium tetrachloride, 2-aminoterephthalic acid, N, N-dimethylformamide and glacial acetic acid. Reagents for antioxidant and whitening activity assays involved DPPH, ABTS, tyrosinase and L-tyrosine. Main instruments included an ultrasonic extractor, ultraviolet-visible spectrophotometer, thermostatted oscillating adsorption device, solvothermal reaction autoclave, Fourier-transform infrared spectrometer, scanning electron microscope and high-speed centrifuge.

2.2. Experimental Procedures

The rutin standard curve was plotted via the sodium nitrite-aluminum nitrate colorimetric method to establish a quantitative determination method for total flavonoids in Angelica dahurica. Total flavonoids were ultrasonically extracted with 70% ethanol, and the crude flavonoid solution was obtained after centrifugation and filtration for content measurement. The optimal macroporous resin was screened through static adsorption experiments, and process parameters including sample loading concentration, flow rate and eluent concentration were optimized. After impurity removal, elution, concentration and drying, preliminarily purified sample Group A was prepared, whose purity and recovery rate were determined. UiO-66-NH_2 was synthesized by the solvothermal method, and the pure-phase material was obtained after washing and activation. FT-IR and SEM were adopted to characterize the chemical structure and micromorphology of the material. A simulated mixed solution containing flavonoids, proteins and pectin was prepared to carry out selective adsorption, adsorption kinetics and four-cycle regeneration experiments, so as to evaluate the adsorption performance and structural stability of the material. High-purity flavonoid sample Group B was prepared by further deep refining of crude flavonoids from Group A with UiO-66-NH_2, and the differences in purity and recovery rate between the two groups were compared. Finally, DPPH and ABTS radical scavenging assays, tyrosinase inhibition assays, as well as moisture absorption and retention tests were performed to comprehensively evaluate the in vitro activity and application performance of flavonoids before and after purification.

3. Results

3.1. Quantitative Determination System of Total Flavonoids Based on Rutin Standard Curve

Ultrasonic extraction with 70% ethanol effectively released flavonoid active components, and the total flavonoid concentration in crude extract could be accurately calculated via the standard curve. It was found that the crude extract contained abundant macromolecular impurities such as pectin and protein, which interfered with subsequent adsorption and purification and exerted adverse effects on flavonoid separation efficiency.

3.2. Screening of Macroporous Resins and Properties of Preliminarily Purified Sample Group A

The resin with optimal comprehensive adsorption and desorption performance was selected as the primary purification medium through comparison among five macroporous resins. After parameter optimization and purification treatment, crude flavonoid Group A was obtained. The macroporous resin effectively removed most strongly polar macromolecular impurities to realize preliminary enrichment of flavonoids with stable recovery rate. Nevertheless, limited by non-specific adsorption mechanism, the resin failed to eliminate trace impurities with similar polarity, resulting in low purity of Group A that could not meet the standard for medicinal skin care raw materials.

3.3. Structural Characterization and Adsorption Performance of Solvothermally Synthesized UiO-66-NH_2

FT-IR results verified that amino groups were successfully grafted onto the material framework, confirming the successful preparation of modified UiO-66-NH_2. SEM images revealed uniform particle size and developed pore channels, providing sufficient adsorption sites and mass transfer channels for the adsorption reaction. Selective adsorption tests proved the material possessed outstanding recognition and enrichment ability toward flavonoids and effective rejection of macromolecular impurities. Adsorption kinetics conformed to the pseudo-second-order kinetic model, indicating that adsorption was dominated by chemical bonding interaction. No obvious decline in adsorption capacity was observed after four regeneration cycles, demonstrating stable structure and good reusability.

3.4. Comparison of Purity and Recovery Rate between Two-Step Purified Sample Group A and Group B

The purity of flavonoid Group B obtained after deep refining by UiO-66-NH_2 was significantly higher than that of Group A purified by single resin, with controllable material loss and stable recovery rate during refining. The two-step purification system remarkably improved product purity while ensuring yield, achieving a favorable balance between purification efficiency and economic benefit.

3.5. In Vitro Antioxidant, Whitening, Moisture Absorption and Retention Properties of Two Groups of Flavonoids

In vitro activity tests demonstrated that two-step purified Group B flavonoids possessed superior antioxidant capacity with lower IC_{50} values for DPPH and ABTS radical scavenging and stronger radical elimination ability. In tyrosinase inhibition assay, Group B exhibited more prominent enzymatic inhibitory activity with smaller IC_{50} and better whitening efficacy. Meanwhile, moisture absorption and retention tests under constant temperature and humidity showed that high-purity Group B had slighter overall performance fluctuation and higher stability with balanced moisture absorption and retention effect, making it more suitable for developing topical medicinal skin care and moisturizing raw materials[4].

4. Discussion

Traditional macroporous resins perform non-specific physical adsorption based on polarity differences, which hardly remove trace impurities with similar polarity and easily lead to co-adsorption of flavonoids and impurities, resulting in insufficient purification depth. This is the primary reason why the purity of preliminarily purified sample Group A fails to meet the standard for medicinal raw materials. In this study, a two-stage purification system was constructed with UiO-66-NH_2 to realize deep refining of total flavonoids from Angelica dahurica through the synergistic effect of targeted hydrogen-bond adsorption and molecular sieve screening. The amino groups on the material surface act as hydrogen bond acceptors and form reversible specific interactions with phenolic hydroxyl groups of flavonoids to selectively capture flavonoid components. The adsorption kinetics conform to the pseudo-second-order kinetic model, verifying that the adsorption is dominated by chemical bonding, which is essentially different from van der Waals force-driven physical adsorption of

conventional resins. The pore size of UiO-66-NH_2 is between the molecular size of flavonoids and the particle size of macromolecular impurities such as pectin and protein, so small-molecule flavonoids enter pore channels for adsorption while macromolecular impurities are intercepted and separated. Amino modification does not damage the rigid zirconium-based framework; the adsorption capacity of the material has no obvious decline after four adsorption-desorption cycles, showing favorable stability and reusability for deep purification of flavonoids[5].

Simultaneous improvement in purity and bioactivity of flavonoids after two-step purification originates from sufficient exposure of active functional groups after impurity removal. Residual macromolecular impurities such as protein and pectin in unrefined Group A randomly wrap flavonoid molecules to produce obvious steric hindrance, shielding phenolic hydroxyl active sites responsible for pharmacological effects, greatly reducing the effective binding efficiency between flavonoids and free radicals or tyrosinase and weakening antioxidant and whitening activities[3]. After deep purification by UiO-66-NH_2, trace and macromolecular interfering impurities are thoroughly eliminated, flavonoid molecules disperse evenly and phenolic hydroxyl sites are fully released to optimize overall sample performance at the micro level. For antioxidant property, exposed phenolic hydroxyl groups rapidly donate protons to neutralize unpaired electrons of DPPH and ABTS free radicals, terminate lipid peroxidation chain reaction, elevate radical scavenging efficiency and significantly lower antioxidant IC_{50} of refined Group B. For whitening activity, free phenolic hydroxyl groups strongly compete with the active center of tyrosinase, the rate-limiting enzyme in melanin synthesis, inhibit catalytic transformation of L-tyrosine to melanin precursors, block melanin synthesis pathway and greatly enhance whitening efficacy. Besides, high-purity flavonoids construct stable hydrogen-bond hydration network with water molecules to achieve more balanced and stable moisture absorption and retention performance, better meeting the application requirements of medicinal skin care raw materials.

The two-step purification process developed in this study matches the positioning of Drug Development Research focusing on pharmaceutical development, applicable to small-batch preparation, pharmacodynamic verification and pre-formulation research of medicinal skin care raw materials with prominent green industrialization advantages. The whole process adopts 70% ethanol as extraction and elution solvent, categorized as Class III low-toxic reagent in pharmacopoeia with high biocompatibility and low solvent residue risk that satisfies quality control criteria for medicinal raw materials. Waste eluent can be recycled after atmospheric distillation to cut production cost and organic wastewater discharge, conforming to the green production concept in pharmaceutical industry. UiO-66-NH_2 is facile to regenerate via ethanol elution for four stable adsorption cycles. Compared with disposable macroporous resins, it effectively lowers consumable cost and solid waste disposal expenditure. The whole workflow consists of conventional unit operations including adsorption, water washing, gradient elution, concentration and drying, without harsh reaction conditions or high-end precision equipment. The process shows favorable parameter stability and repeatability, easy to scale up from lab scale to small-batch pilot production, providing feasible technical support for pharmaceutical development of high-purity Angelica dahurica flavonoids.

5. Conclusion and Outlook

This study successfully constructed a green two-step purification process combining preliminary enrichment by macroporous resin and deep refining by UiO-66-NH_2 for total flavonoids from Angelica dahurica, effectively overcoming the defects of weak selectivity and low purity in traditional resin purification. Relying on dual functions of targeted hydrogen-bond adsorption and molecular sieve sieving, UiO-66-NH_2 accurately enriches flavonoids and removes trace impurities to greatly elevate product purity. Deep purification fully exposes phenolic hydroxyl active sites of flavonoids, remarkably improving antioxidant activity, tyrosinase inhibitory whitening activity and moisture absorption & retention stability to satisfy quality requirements of medicinal skin care raw materials. Featuring safe recyclable solvent, regenerable material, simple and controllable operation, this process fits the scenario of small-batch preparation in pharmaceutical development with remarkable green advantages. Subsequent research can optimize process parameters via an orthogonal

experiment to develop topical flavonoid preparations. Additionally, cellulose can be extracted from Angelica dahurica herb residues to fabricate 3D printing filter materials for solid waste resource utilization, further improving the overall green benefit of the whole process.

Disclosure statement

The author declares no conflict of interest.

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