Processing of waste material of radix physochlainae for preparation of fine chemicals after extraction

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Abstract. Waste residues of Chinese traditional medicine radix physochlainae (Huashanshen) contain a large amount of hemicelluloses after extraction. After the removal of the cellulose and lignin, main components of the solution are different degree of hydrolysis products of hemicelluloses. In the degradation process, hemicelluloses firstly become pentose, and then pentose loses 3 molecules of water and turns into furfural. This study explored a series of conditions of the method; finally the yield of furfural can reach 8.5% (calculated with the weight of raw residues) under the condition of pH of 0.2-0.3, temperature of 104-106°C, hydrolysis duration for 10 minutes. Furfural can be further processed to be resin materials.

1. Introduction
In recent years, with the rapid development of traditional Chinese medicine and natural medicine industry, the use of herbal raw materials is increasing significantly. However, there exists the problem of the low utilization ratio of Chinese herbal medicines, and related enterprises produce a large amount of herbal residue every year, which is about 70% weight of the total amount of raw material. More than 90% manufacturers directly treat it as an industrial waste. The popular treatment mainly includes piling, burying or burning, which will not only pollute the environment, but also cause the waste of resources. According to the domestic and foreign experience, the treatment of organic solid waste should be based on resource utilization, which can realize the harmless reduction of waste material [2]. The residue always contains a large amount of crude fiber, lignin and hemicelluloses, and the degradation and transformation of application can reduce the environmental pollution and improve utilization ratio for renewable resource. As an example, radix physochlainae is a common alkaloids-rich herb used as traditional medicine, which has the clinical effects to warm lung phlegm, relieve cough and asthma, and tranquilize the mind [3]. Based on the waste residue after the extraction of bioactive ingredients, the study firstly removed cellulose and lignin effectively through appropriate pretreatment, and then the obtained hemicelluloses with different hydrolysis degree was hydrolyzed to prepare furfural with degradation process catalyzed by sulfuric acid. Furfural can be further processed to be resin materials. It can be a good way to overcome the shortcomings including low utilization of raw materials and high energy consumption.

2. Experimental
2.1. Materials, reagents and instrument
Radix physochlainae (Huashanshen) was purchased from Xindu herbal market, Chengdu. Sulfuric acid, furfural and chloroform were purchased from Chengdu Hangjia chemical reagent. Moreover, the
electrical heating sleeve, DF-101D type constant temperature magnetic stirrer (Gongyi Yuhua Instrument Co. Ltd), MODEL-3 rotary evaporator (Shanghai Yarong biochemical instrument factory), SHZ-D (III) circulating water vacuum pump (Gongyi Yuhua instrument factory), TU1800 UV spectrophotometer (Beijing Puxi General Instrument Corp) and XH-MC-1 microwave reactor (Beijing Xianghu science and Technology Development Co Ltd) were used.

2.2. Standard curve of furfural

In the wavelength range of 200–600 nm, its maximum absorption wavelength of furfural was at 276 nm as shown in Fig.1(a). 0.0625 g authentic compound of furfural was weighed and dissolved in distilled water, and then transferred to a 100 mL volumetric flask with a pipette. After being diluted to 100 mL, the concentration of 6.25 μg/mL standard solution of furfural was obtained. 1 mL~10 mL of standard solution was further diluted to 10 mL, and 0.625 μg/mL, 1.250 μg/mL, 1.875 μg/mL, 2.500 μg/mL, 3.125 μg/mL and 3.750 μg/mL work solutions were prepared, respectively. Distilled water was used as the reference solution. According to the principle of least squares, the relationship of absorbance data (y) and concentration (x) of furfural was fitted and the standard curve is shown in Figure 1(b), the regression equation is \( y=0.1626x - 0.0042 \) and \( R^2=0.9998 \). The results showed that furfural solution showed good linear relationship in the concentration range of 0.625 μg/mL~3.750 μg/mL.

![Fig. 1 UV full length scanning result (a) and standard curve (b) of furfural](image)

2.3. Processing procedures

(1) Dry radix physochlainae (Huashanshen) was grinded to100 mesh, and then refluxed with 95% ethanol (ratio of mass to volume=10, g/mL) for 1 hour each time. The process was repeated 3 times to extract those useful bioactive compounds thoroughly. The waste materials were collected by filtration.

(2) 10 g dry waste residue of radix physochlainae after pretreatment was weighed and placed in the flask, and then 8% NaOH solution with the 20:1 ratio of liquid to solid (mL/g) was added and reacted under stirring for 8 h under 60°C. After cooled to room temperature, the reaction system was filtered under vacuum and concentrated sulfuric acid was used to adjust the pH value of the filtrate to 2, the precipitation process was carried out on 30°C for one hour and the solid was removed by centrifugation with the speed of 500 rpm. (3) The supernatant was further mixed with 2 mol/L sulfuric acid to pH 0.2. The solution was transferred to the 1000 mL three neck flask and reacted under magnetic stirring and the increasing speed of temperature was controlled. The reaction system reached the refluxing temperature after a certain period of time. (4) The system was maintained under the refluxing temperature. After a certain period of time, furfural began to be generated in the system, which was collected through steam distillation in the end.

3. Results and discussion

3.1. Effect of dehydration time
Through two steps pentosan can be dehydrated to furfural; in the first step pentosan is dehydrated to become pentose with high yield and speed [4]. Compared with other studies [5,6], although this experiment employed one-pot method, the reaction substrate was no longer a pentosan-rich plant. After treatment of the first two steps in above processing procedure, most of the cellulose and lignin have been removed effectively, and the obtained solution was mainly composed of polypentose molecules with different degree of polymerization. So it can be considered to shorten the time of hydrolysis in the first step. On the other hand, the chemical stability of furfural is poor, and it is easy to be oxidized to produce bran acid; all of light, heat and air may cause the oxidation. The system of furfural production is acidic and the temperature is also high. If furfural is not immediately separated from the system, it will produce by-products, which can be found as the black material in the bottle wall. Therefore, it should be appropriate to shorten the time of dehydration. In order to determine the optimum conditions for the production of furfural, the time range of hydrolysis from 0 min to 40 min (from the start of the refluxing) was investigated. According to the experimental results, the dehydration time is suitable for 10 min, which can avoid the oxidation of furfural in the acidic environment. After the time more than 10 minutes, the yield did not continue to rise significantly, and with the extension of time more and more black jelly began to generate and adhere to the wall of the bottle, which is the by-product of oxidation of furfural. Therefore, it is advisable to keep the degradation process for 10 min after reaching the refluxing status (104~106°C).

3.2. Effect of distillation time
In the stage of steam distillation, on the one hand, the steam refluxing temperature is higher than the system temperature, which is conducive to the formation of furfural; on the other hand, steam will take furfural out of the system timely to avoid its oxidation in acidic condition under high temperature. In the study, the water vapor condensed liquid was collected; as the result, a total of 10 equivalent fractions were obtained and each fraction was 250 mL (about 30 min). According to the results of quantitation, furfural content and cumulative furfural production were shown in Figure 2(a) and 2(b). From the experimental results, it can be seen that the yield of furfural in individual fractions appears a sharp decline after No.7, and in the tenth fraction of furfural content already becomes very low. The whole trend is to increase first and then decrease. For the economic consideration, 9×250 mL of distillation liquid is more reasonable for the efficient collection of furfural. The average yield of furfural was 8.5%.

![Fig. 2 Furfural content in each fraction (a) and accumulative total of furfural in steam distillation (b)](image)

3.3. Separation of furfural product
The distillation liquid of furfural solution was collected and combined. On the basis of the great difference of furfural solubility in aqueous solution under different temperature, the furfural product can be separated. Especially, for the existence of the large amount of salt produced in the front steps of pH adjustment, the aqueous solution is almost saturated, which can further reduce the solubility of furfural in aqueous solution after cooling. As the result, furfural exists in the upper layer, and it can be obtained by separating funnel. Residual furfural in aqueous solution was detected by UV, and the recovery rate was calculated as 68.44%. Although furfural extraction from aqueous solution cannot be
completely, more than half of the furfural can be obtained through the liquid; meanwhile it reduces the amount of furfural in aqueous solution and the throughput of distillation.

3.4. Microwave assistance
Microwave radiation can pass through the microwave-transparent solvents freely and then arrive at the inner parts of plant materials, resulting in a sudden rise of temperature in related system. Continuous high temperature will make internal pressure exceed the expansion capacity of cell wall, which can greatly accelerate the degradation rate and enhance degradation efficiency obviously. On the basis of previous research, this study investigated the effects of different power of microwave on the yield of furfural by using 100 ~ 900 W adjustable microwave reactor. It was found that the yield of 8%~9% was also achieved within 6~7 min when 500 W assisted microwave was used to help catalytic degradation. However, if the microwave power is too great, the local temperature will be over high, which can easily result in severe carbonation of raw materials and the significant increase of production of byproducts. The technology is proved to be an important method for the degradation of herbal residues, and it can be also taken into consideration in the process of extraction.

3.5. Further processing for resin material
In order to evaluate the applicability of this kind of furfural product prepared from herbal materials, resin material was selected as an object in the section. Furfural resin is a kind of polymer which can be obtained by condensation polymerization or copolymerization with furfural as the main raw material. It has high temperature resistance, good chemical resistance and electrical insulation, and can be used in the production of tube plates, machinery parts and equipment lining coating, etc. We firstly used furfural to form a linear polymer under acid catalysis, and then double bond polymerization continues to occur in the presence of acid. Finally, the insoluble and non-fused cross-linked polymer can be obtained. The resin product is a black sticky liquid, which can become solid after the hardening treatment with benzene sulfochloride or p-toluene sulfonic acid. The result indicated the self-made furfural from waster residue had good property in above processing process.

4. Summary
In the extraction process, herbal medicine has experienced a series of grinding, swelling and breaking of cell processes (especially in the use of novel solvents just like ionic liquids in recent years, which have strong influence on the herbs skeleton), which is very conducive to the further processing. The corresponding residues always contain a large amount of crude fiber, lignin and hemicelluloses, and the degradation and transformation can be applied to prepare high value-added products and reduce environmental pollution effectively. This paper developed an easy and feasible way to exploit the roots of the herbal material, meanwhile provided a meaningful reference for similar studies.

References
[1] Shi L C, Ye C and Li X 2012 Treatment method and comprehensive utilization of drug residues in traditional Chinese medicine production enterprises Guide of China Medicine 10 385-386.
[2] Zhen G M and Huang G H 2006 Biology and control of compost environment, Science Press, Beijing
[3] National Pharmacopoeia Commission, 2010 China Pharmacopoeia (2010 edition), China Medical Science and Technology Publishing House, Beijing
[4] Xu J, Xiao C H and Hui Y H 2010 Production technology of furfural and its prospect Journal of Puyang Vocational and Technical College 23 150-152.
[5] Li Z S and Yi W G 2010 Study on furfural preparation from corn cob, Fine Chemical Intermediates 404 53-55.
[6] Xu G F, Lin W and Cai L X 2010 Studies on furfural production with wheat stalk. Journal of Putian University 17 75-77.