INFLUENCE OF PRE-TREATMENT ON ENZYMATIC DEGUMMING OF APOCYNUM VENETUM BAST FIBERS IN SUPERCRITICAL CARBON DIOXIDE

by

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Pre-treatment of apocynum venetum bast fibers in supercritical carbon dioxide can improve the efficiency of enzymatic degumming of apocynum venetum bast fiber. This paper studies experimentally effect of pressure and degumming time on degradation rate, the results can be used for optimal design of degumming.

Key words: *apocynum venetum, supercritical carbon dioxide, pretreatment, degumming, swelling*

Introduction

Apocynum venetum (AV) is a type of wild perennial shrub, which contains up to 50-60% of incrusting non-cellulosic gummy material consisting mainly of pectin, hemicelluloses and lignin waxes, and fats bind the fiber bundles together in a composite-like structure. The plant gum must be eliminated for further industrial utilization. The conventional degumming process which was carried out in a hot alkaline solution would damage AV fibers and influence spinning and weaving processes. Therefore, this degumming process will not only consume large amount of chemicals and energy but also bring serious environmental pollution [1, 2]. Besides, biotechnological degumming involving polysaccharide degrading microorganisms and enzymes is another way to remove the plant gum [3], however it is time-consuming. Thus, a new degumming method is strongly needed to overcome the above mentioned shortcomings. As an environmental friendly medium, supercritical carbon dioxide (SC-CO_2) has obtained numerous achievements in the field of extraction due to its non-toxicity, non-explosive and easily being removed from the obtained products-extracts, thus allowing the preparation of solvent-free extracts [4, 5]. Stamenic *et al.* [6] and Vidović *et al.* [7] found that the pre-treatment of plant materials played important roles in the extraction in SC-CO_2, and the swelling of *herbaceous matrix* exposed to SC-CO_2 greatly enhanced diffusion process. The research showed that pre-treatment of herbal material to be extracted can change the "direction of extraction process" which results in higher extraction yields. Meanwhile, studies also confirmed ultra-sound pre-treatment of fibers in SC-CO_2 had positive influence on the efficiency of supercritical extraction [8, 9]. Based on the similar removal mechanism of supercritical fluid extraction, supercritical fluid enzymatic degumming is one of SC-CO_2 degumming which can be regarded as another application of SC-CO_2 extraction. Yang *et al.*

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[10] investigated the enzymatic degumming of ramie in SC-CO_2. The result showed that when un-pretreated ramie was degummed for 3 hours, the gum removal rate reached 17.2%. It indicated the enzymatic degumming method needs long time. Here, the present study is to investigate the influence of pretreatments on enzymatic degumming of AV bast fiber in SC-CO_2 and to improve the efficiency of enzymatic degumming of AV bast fiber.

Experiments

Materials

One-year old AV bast fibers were obtained in Xinjiang province, China. The bast fibers were decorticated from the pith tissue by hand. The gum content of the AV bast fibers was 58.36%. Carbon dioxide (CO_2) (purity > 99.99%) was purchased from Zhonghao Guangming Research & Design Institute of Chemical Industry Corporation. SC-CO_2 fluid apparatus (TharSFC) was from Waters Company (USA).The pectinase was purchased from Ruiyang Biotech Co., Ltd. (China). All chemicals used in this study were of analytical reagent grade (Sinopharm Chemical Reagent Co. Ltd., China).

Pretreatment in SC-CO_2

The pretreatment process was performed under the pressure of 25 MPa and at the temperature of 40 °C. The CO_2 flow rate was set as 20 g per minute with reaction time 60 minutes. Ethanol and water (v/v = 7/3) were used as co-solvents.

Enzymatic degumming in SC-CO_2

Pectinase was dissolved in water with weight ratio of 1:100 (pectinase/water), which was used as co-solvents. The enzymatic degumming process was performed under the pressure ranging from 15 MPa to 20 MPa and at the temperature of 50 °C. The CO_2 flow rate was set as 20 g per minute with reaction time ranging from 10 min to 90 min.

Analysis of AV bast fiber

The degradation rate of the AV bast fibers was calculated as:

$$\text{Degradation rate } (\%) = \frac{G_0 - G_r}{G_0} \times 100 \tag{1}$$

where G_0 is the weight of AV bast fibers before degumming, and G_r – the weight of the AV bast fibers after degumming.

Results and discussions

Mass balance

The model of mass transfer was given by Stastova *et al.* [11]. Under the condition of constant temperature and pressure, SC-CO_2 (mass flow rate, Q) flows through the AV bast fibers (quality, N) in reaction kettle with the form of horizontal pushing. If the axial dispersion and the accumulation of solute in solvent are negligible, the mass balance for an element of volume is given as:

$$-(1-\varepsilon)\rho_s \frac{\partial x}{\partial t} = J(xy) \tag{2}$$

$$(1-\varepsilon)\rho_s \frac{Q}{N}\frac{\partial y}{\partial t} = J(xy) \tag{3}$$

where ε is the void fraction, ρ [kgm^{-3}] – the density, x [kgkg^{-1}] – the solid-phase concentration, y [kgkg^{-1}] – the solvent-phase concentration, J [kgm^{-3}] – the mass transfer rate, h – the dimensionless axial co-ordinate ($0 \le h \le 1$), and subscript s – the solid phase.

If the solvent is solute-free at the entrance of the reaction kettle and all particles have the same initial solute content x_0. The boundary conditions are:

$$x(h, t=0) = x_0, \qquad y(h, t=0) = 0 \tag{4}$$

and the mass removed from the AV bast fibers equals to:

$$E = Q\int_0^1 y(h=1, t)\mathrm{d}t \tag{5}$$

where E [kg] is the mass removed from the AV bast fibers.

In the first stage of degumming, the degumming rate was controlled by its diffusion and convection in the solvent, mass transfer rate can be expressed as:

$$J(x, y) = k_f a \rho_f (y_r - y), \qquad x > (1-G)x_0 \tag{6}$$

The second stage of degumming starts when the easily accessible gum has been removed. The rate of degumming depends now on the diffusion of solute from the interior of the plant tissue to the surface:

$$J(x, y) = k_s\ a\ \rho_s (x - x^+), \qquad x \le (1-G)x_0 \tag{7}$$

where k [ms] is the mass transfer coefficient, y_r [kgkg^{-1}] – the solubility, subscript f – the solvent phase, and subscript + is for interfacial boundary.

Equations (2)-(7) can be integrated numerically to obtain the mass of degumming:

$$Z = \frac{Nk_f a \rho_f}{Q(1-\varepsilon)\rho_S}, \qquad Y = \frac{Nk_s a x_0}{Q(1-\varepsilon)y_r} \tag{8}$$

where Z is the parameter of the first degumming period, and Y – the parameter of the second degumming period.

Effect of degumming time on degradation rate

The effect of degumming time (in the range from 10 minutes to 90 minutes) on the degradation rate was shown in fig. 1. It can be observed that the effect of the two degumming methods was very obvious in the first stage. Firstly, the possible reason was that the inorganic and soluble substances in AV bast fibers easily dissolved and precipitated. Secondly, pectinase easily degradated the pectin on the surface of bast fibers. In the assumption of the eq. (6) and eq. (7), $K_s \le K_f$, the mass transfer rate of the first stage was high and the removal of gum was fast, which was consistent with the experimental results. In the process of degumming

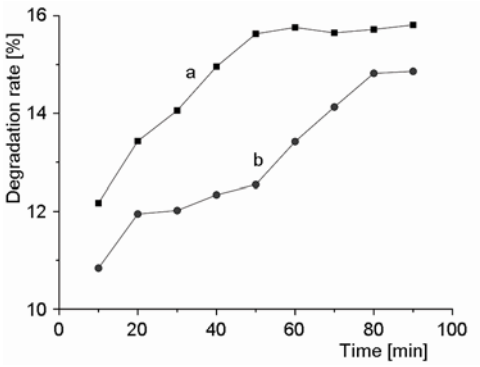

Figure 1. Effect of degumming time on degradation rate; (a) pretreated, and (b) un-pretreated

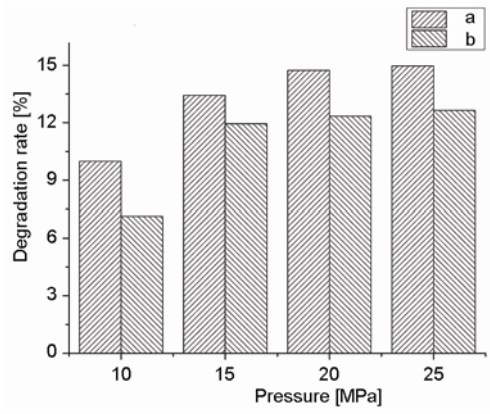

Figure 2. Effect of pressure on degradation rate; (a) pretreated, (b) un-pretreated

utilizing pectinase in SC-CO_2, the degradation rate of pretreated AV fibers was lineally related with the treated time (10 minutes to 50 minutes). The degumming loss reached 15.63% within 50 minutes. However, the un-pretreated AV fibers did not exhibit the same results. The degradation rate had small changes in the time of ranging from 20 minutes to 50 minutes. After 50 minutes, the degradation rate increased rapidly, the degradation rate reached 14.82% at 80 minutes. The reason of degradation rate could be that the swelling of AV bast fibers occurred after being pretreated. Swelling increased void fraction (□), decreased density (ρ) of AV bast fibers, and accelerated the efficiency of degumming. To the un-pretreated AV fibers, the possible reason for the increase of degradation rate was that the swelling of AV bast fibers occurred at 50 minutes, therefore, the degradation rate increased significantly. After the degumming was completed, the degradation rate of pretreated AV fibers was higher in comparison with the untreated fibers. The phenomenon can be explained that the partial swelling occurred after decompression. Thus, the pretreated AV fibers exhibited larger swelling, more voids and higher degradation rate.

Effect of pressure on degradation rate

Experiments to investigate the effects of pressure on degradation rate were planned by following pressure from 10 MPa to 25 MPa and the results were shown in fig. 2. Under the same condition, an increase of pressure resulted in the increase of degradation rate. When pressure exceeded 20 MPa, there were unobvious changes in degradation rate. For this phenomenon, the reason was that the density of CO_2 and the ability of dissolving solute increased but the diffusion coefficient decreased slightly with increasing the pressure. Therefore, it was concluded that the proper pressure for enzymatic degumming was 20 MPa. The degradation rate of the pretreated AV bast fibers is higher than the un-pretreated under different pressures, which also indicated that the swelling of AV bast fibers occurred after pretreatment.

Conclusions

This paper reported the influence of pretreatments on enzymatic degumming of AV bast fibers in SC-CO_2. The experimental results showed that the effect of pre-treated on degumming was very obvious. The obtained results showed that the pre-treatment of AV bast fibers leaded to partial swelling of them, which would lead to increase void fraction and diffusion coefficient, decrease density of AV bast fibers, and finally accelerate the efficiency of

enzymatic degumming. Because of the partial swelling occurred after decompression, when the degumming was completed, the degradation rate of pre-treated AV fibers was higher in comparison with the un-pretreated fibers. Therefore, the pre-treatment of AV bast fibers plays an important role in the efficiency of enzymatic degumming.

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Reference

[1] Li, Z. L., Yu, C. W., Effect of Peroxide and Softness Modification on Properties of Ramie Fiber, *Fibers and Polymers, 15* (2014), 10, pp. 2105-2111
[2] Parikh, D. V., *et al.,* Improved Chemical Retting of Kenaf Fibers, *Textile Research Journal, 72* (2002), 7, pp. 618-624
[3] Yu, H. Q., Yu, C. W., Influence of Various Retting Methods on Properties of Kenaf Fiber, *The Journal of The Textile Institute, 101* (2010), 5, pp. 452-456
[4] Seabra, I. J., *et al.,* Statistical Mixture Design Investigation of CO_2–Ethanol–H_2O Pressurized Solvent Extractions from Tara Seed Coat, *Journal of Supercritical Fluids, 64* (2012), Apr., pp. 9-18
[5] Heidaryan, E., *et al.,* Viscosity of Pure Carbon Dioxide at Supercritical Region: Measurement and Correlation Approach, *Journal of Supercritical Fluids, 56* (2011), 2, pp. 144-151
[6] Stamenic, M., *et al.,* Swelling of Plant Material in Supercritical Carbon Dioxide, *Journal of Supercritical Fluids, 52* (2010), 1, pp. 125-133
[7] Vidović, S. *et al.,* Influence of Pre-Treatments on Yield, Chemical Composition and Antioxidant Activity of Satureja Montana Extracts Obtained by Supercritical Carbon Dioxide, *Journal of Supercritical Fluids, 95* (2014), 11, pp. 468-473
[8] Meyer, F., *et al.,* Effect of CO_2 Pre-Treatment on scCO_2 Extraction of Natural Material, *Chemical Engineering and Processing: Process Intensification, 56* (2012), 2, pp. 37-45
[9] Riera, E., *et al.,* Mass Transfer Enhancement in Supercritical Fluids Extraction by Means of Power Ultrasound, *Ultrason Sonochem, 11* (2004), 3-4, pp. 241-244
[10] Yang, X. A., *et al.,* Supercritical CO_2 Enzymatic Degrading of Ramie Gelatin and Testing Degradation Products, *Journal of Textile Research, 30* (2009), 5, pp. 82-87
[11] Stastova, J., *et al.,* Rate of the Vegetable Oil Extraction with Supercritical CO_2-III. Extraction from Sea Buckthorn, *Chemical Engineering Science, 51* (1996), 18, pp. 4347-4352

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