INVESTIGATION OF THE OPTIMAL TREATMENT CONDITION FOR FLAX ROVE IN SUPERCRITICAL CO_2

by

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Original scientific paper
https://doi.org/10.2298/TSCI1804613Z

Three treatment parameters of supercritical CO_2 have been optimized by a response surface method using central composite design to obtain isolate yield of flax rove. Influence of operating parameters including dosage of cellulase, temperature, and pressure on final response is evaluated. The results show that the experimental values are adequately fitted to a quadratic polynomial equation. The optimal isolate yield is obtained with 2% cellulase dosage under temperature of 50 °C and pressure of 20 MPa. Mathematical model is also applied to describe the kinetic behavior of the treatment process, revealing that supercritical CO_2 is a promising green solvent for the scouring and bleaching of flax rove.

Key words: *supercritical CO_2, response surface method, treatment, flax rove, kinetic behavior*

Introduction

Flax fibers, one of the most important sources of textile plant fibers, are being re-evaluated thanks to the unique features of freshness, comfort, and elegance of linen textiles such as apparels, sheets, towels, and other household textile items [1]. Flax fibers, besides cellulose (65-80%), contain non-cellulosic substances such as hemicellulose and lignin [2]. In order to remove the non-cellulosic gummy materials, coloring, and was-like impurities from flax, gray flax fabrics are subjected to pretreatment process including scouring, desizing and/or bleaching [3]. Apart from the recently developed enzymatic treatments, sodium hydroxide is the most commonly used chemical for scouring of flax rove while hydrogen peroxide is the widely used bleaching agent [1]. There is an increasing demand for a novel clean treatment method which can be applied easily and efficiently to flax rove as the pollution from alkaline treatment was left as an open question. To the authors' knowledge, no published report fully describes that the flax rove was treated with cellulase in supercritical CO_2.

The aim of this work was to investigate the scouring and bleaching of flax rove with cellulase at different conditions in supercritical CO_2. The effects of major process parameters including dosage of cellulase, temperature, and pressure on the isolate yield of flax rove were studied using the response surface methodology (RSM). A suitable quadratic polynomial

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model was established to fit with the experimental data. Moreover, extended Lack's plug flow model was used to study the scouring and bleaching of flax rove in supercritical CO_2.

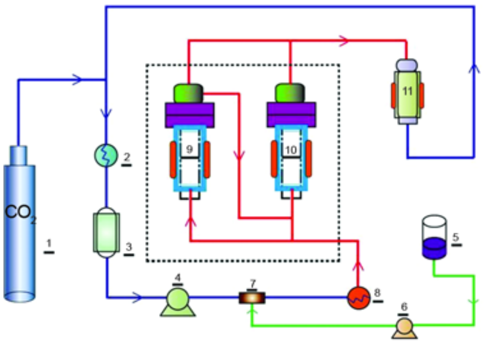

Figure 1. Schematic diagram of supercritical CO_2 fluid treatment apparatus; *(1) CO_2 tank, (2) purifier, (3) refrigerator, (4) high-pressure pump, (5) co-solvent tank, (6) co-solvent pump, (7) dynamic mixer, (8) heat exchanger, (9) treatment kettle I, (10) treatment kettle II, and (11) separator (for color image see journal web site)*

Experimental

Materials

Natural flax roves (6 twist per m) were provided by Jiaxing Unbleached Linen Textile Co., Ltd., China. Cellulase was purchased from Jiangsu Ruiyang Biotech Co., Ltd., China. The CO_2 gas (99.9%) used in all of the experiments was purchased from Zhonghao Guangming Research & Design Institute of Chemical Corporation, China.

Supercritical CO_2 scouring and bleaching

Flax rove was treated with cellulose by supercritical CO_2 in a batch system as shown in fig. 1. In this apparatus, flax rove was placed into a treatment vessel and sealed. Before treatment, CO_2 was firstly heated to above the critical temperature with a heat exchanger and was pressurized to above the critical pressure using a high pressure pump [4-7]. Supercritical CO_2 was then injected to the treatment vessel in which flax rove would be treated. After treatment, supercritical CO_2 was separated in a separator vessel and stored in a CO_2 storage vessel for reuse. The treatment experiments were conducted with dosage of cellulase (1% to 5%) at temperatures and pressures ranging from 30 °C to 70 °C and 10 MPa to 30 MPa, respectively. The flax rove was then removed and used for further analysis after the process was finished.

Response surface methodology

In general, RSM consists of a group of mathematical and statistical techniques that match empirical models to experimental data [8]. The RSM is a useful tool for analyzing the relationships between measured responses and factors (independent variables) [9]. In this work, the influences of three factors, namely dosage of celllulase, temperature, and pressure were studied on treatment of flax rove in supercritical CO_2. The operating conditions were varied at 5 levels, as shown in tabs. 1. and 2 lists the complete design matrix with coded levels, and actual and predicted responses.

The whiteness, *Y*, was assumed to be affected by three independent variables (ζ_1: dosage of cellulase, ζ_2: temperature, and ζ_3: pressure) and is represented:

$$Y = f(\xi_1, \xi_2, \xi_3) \tag{2}$$

The whiteness was analyzed by a response surface method to fit a second-order polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum_{i=1}^{2} \sum_{i=i+1}^{3} \beta_{ij} x_i x_j + \varepsilon \tag{3}$$

Table 1. Coded and uncoded levels of independent variables

Variable	Symbol coded	Levels				
		–2	–1	0	1	2
Dosage of cellulase [%]	x_1	1	2	3	4	5
Temperature [°C]	x_2	30	40	50	60	70
Pressure [MPa]	x_3	10	15	20	25	30

Table 2. Experimental variables and responses

Run	x_1	x_2	x_3	Isolate yield [%]	
				Actual	Predicted
1	0	0	0	43.1	42.2
2	0	0	0	39.2	35.3
3	0	–1.68	0	28.3	26.8
4	1	1	–1	31.4	29.3
5	0	0	0	40.3	38.6
6	1	1	1	35	36.2
7	1.68	0	0	39.2	39.9
8	–1	–1	1	28.8	29.5
9	0	0	0	41.8	41.3
10	–1	1	1	32.1	30.2
11	–1	1	–1	27.3	27.9
12	0	0	–1.68	26.5	25.8
13	0	0	0	39.8	38.7
14	0	1.68	0	31.5	32.4
15	0	0	0	39.9	38.5
16	–1	–1	–1	29.6	30.2
17	–1.68	0	0	31.2	32.1
18	1	–1	–1	26.7	27.8
19	1	–1	1	29.7	28.6
20	0	0	1.68	35.6	36.2

where β_0 is a constant, β_i, β_{ii}, and β_{ij} are linear, quadratic, and interactive coefficients, respectively, ε represents the error term, x_i and x_j are independent variables which are related to the original variable, ζ, as:

$$x = \frac{\text{original variable} - \text{midpoint of original interval}}{\text{interval of original range}} \tag{4}$$

The experiments were designed using design expert software. Analysis of variance (ANOVA) was used to determine the significance of the model through regression and mean square of residual error. The coefficient of determination, R^2, was used to assess the quality of the developed model.

Result and discussion

Response surface analysis

Effects of dosage of cellulase, temperature, and pressure on the isolate yield of flax rove were investigated in supercritical CO_2. Multiple regression was used to analyze the isolate yield from the 20 runs which were generated by the RSM, tab. 2. The experimental data were analyzed using the analysis of variance to assess the *goodness of fit*, as listed in tab. 3. The probability, p, value of the quadratic model was less than 0.0001, which showed an excellent fit and appeared to reasonably represent the data. After examining the lack of fit, a quadratic model was found to be adequate to explain the relationship between the isolate yield and the treatment parameters. However, the coefficient of determination, R^2, should also be taken into consideration when verified the model. The R^2 value at 0.9355 is considered very excellent, indicating that 93.55% of the variables could be explained by the quadratic model. It can be clearly inferred from R^2 value that the model was significant and extremely appropriate for the present experiment results.

Regression coefficients were determined to predict the polynomial model for the isolate yield, and eq. (5), expressed in coded variables, were obtained:

$$y = 0.41 + 0.0014x_i + 0.012x_2 + 0.019x_3 - 0.022x_2^2 - 0.041x_2^2 - 0.037x_3^2 \tag{5}$$

Table 3. The ANOVA for response surface to quadratic model for isolate yield

Source	Coefficient	Sum of square	*df*	Mean square	F-value	P-value	Significance
Model		0.050	9	0.006083	16.1	< 0.0001	**
Constant	0.41						
x_1	0.014	0.002494	1	0.002494	6.6	0.0279	*
x_2	0.012	0.001965	1	0.001965	5.2	0.0457	*
x_3	0.019	0.004914	1	0.004914	13.01	0.0048	*
x_1x_2	0.011	0.001012	1	0.001012	2.68	0.1326	n. s.
x_1x_3	0.00325	0.0000845	1	0.0000845	0.22	0.6464	n. s.
x_2x_3	0.00775	0.0004805	1	0.0004805	1.27	0.2857	n. s.
x_1^2	–0.022	0.007263	1	0.007263	19.23	0.0014	*
x_2^2	–0.041	0.024	1	0.024	64.71	< 0.0001	**
x_3^2	–0.037	0.02	1	0.02	52.57	< 0.0001	**
Residual		0.003778	10	0.0003778			
Lack of fit		0.002695	5	0.000539	2.49	0.1698	n. s.
Pure error		0.001083	5	0.0002166			
Core total		0.059	19				

* $p < 0.1$; n.s.: not significant; ** $p < 0.001$.

According to eq. (5), the isolate yield of flax rove depends on the linear effects of dosage of cellulase, x_1, temperature, x_2, pressure, x_3, the quadratic effect of dosage of cellulase, x_1^2, the quadratic effect of temperature, x_2^2, and the quadratic effect of pressure, x_3^2. Linear terms x_1, x_2, and x_3 indicated a positive effect while quadratic term x_1^2, x_2^2, and x_3^2 indicated a negative effect.

Mathematical modeling of the supercritical CO_2 scouring and bleaching

Mathematical model is effective to determine the isolate yield and mass transfer parameters, finally to optimize the scale-up process. In this section, the extended Lack's plug flow model proposed by Sovova was used to study the scouring and bleaching of flax rove in supercritical CO_2 [10]. The mathematical model depends on many factors, and dosage of cellulase, temperature and pressure are used to establish the differential equations for the mass balance in the fluid phase. According to the differential mass balance equations for the solid and fluid phases, the following expressions were used to describe the isolate yield of flax rove during three different periods in supercritical CO_2:

$$e = \begin{cases} q y_r \left[1 - \exp(-z)\right] & q < q_m \\ y_r \left[q - q_m \exp(z_w - z)\right] & q_m \le q < q_n \\ x_0 - \left(\dfrac{y_r}{w}\right) \ln\left\{1 + \left[\exp\left(\dfrac{w x_0}{y_r}\right) - 1\right] \exp\left[w\left(q_m - q\right)\right] \dfrac{x_k}{x_0}\right\} & q_n \le q \end{cases} \tag{6}$$

where

$$q_m = \frac{x_0 - x_k}{y_r z} \tag{7}$$

$$q_n = q_m + \frac{1}{w} \ln\left[\frac{x_k + (x_0 - x_k)\exp\dfrac{w x_0}{y_r}}{x_0}\right] \tag{8}$$

$$\frac{z_w}{z} = \frac{y_r}{w x_0} \ln\left\{\frac{x_0 \exp\left[w(q - q_m)\right] - x_k}{x_0 - x_k}\right\} \tag{9}$$

$$z = \frac{k_\mathrm{f}\, a \rho_\mathrm{f}}{q(1-\varepsilon)\rho_\mathrm{s}} \tag{10}$$

$$w = \frac{k_\mathrm{s} a}{q(1-\varepsilon)} \tag{11}$$

where q_m and q_n are q values when scouring and bleaching of the solute within the flax rove begins and the easily accessible solute is fully treated, q is the specific mass rate of CO_2 fluid; z and w are the dimensionless mass transfer parameters in solid and solvent phases being proportional to the mass transfer coefficients of two phases, z_w – the dimensionless boundary co-ordinate between slow and fast treatment regions, x_0 – the initial total concentration of cellulase, x_k – the initial content of barely accessible solute inside the flax rove, ρ_s and ρ_f are the densities of solid and fluid phase, respectively, ε – the void fraction, a – the specific interfacial area of flax rove, y_r – the isolate solubility in supercritical CO_2, t – treatment time, k_s and k_f are the solid and fluid phases mass transfer coefficients, respectively, x_0 was determined by traditional method [10].

According to the results depicted in tab. 3, the mass transfer coefficient in the fluid phase k_f decreased with the rising pressure because of a reduction in the velocity of supercritical CO_2, which led to the increase of external mass transfer resistance [10, 11]. The increase of CO_2 flow rate resulted in an increase in k_s, indicating that the isolate yield of flax rove was mainly affected by the convection in the fluid phase [12]. The results revealed that the tuning parameters including k_f, k_s, x_k, and y_r were computed by minimizing the errors between the experimental and calculated yield values. The average absolute relative deviation (AARD) was used to evaluate the mathematical model results:

$$\text{AARD}(\%) = \frac{1}{n}\sum_{i=1}^{n}\left(\left|\frac{y_{\text{i,m}} - y_{\text{i,e}}}{y_{\text{i,e}}}\right|\right)\times 100\% \tag{12}$$

where n is the number of experimental data, $y_{\text{i,m}}$ and $y_{\text{i,e}}$ are the isolate yield obtained by the model and the experimental data, respectively.

Conclusions

In this work, supercritical CO_2 treatment was applied to the scouring and bleaching of flax rove. The effects of dosage of cellulase, temperature, and pressure on the isolate yield of flax rove were investigated by using the RSM. The optimal treatment conditions for flax rove were found to be 2%, 50 °C, and 20 MPa by simplified regression equation. The predicted isolate yields by mathematical modeling adequately agreed with the experimental data for all the investigated conditions. The mathematical modeling was a good predictor for the experimental results as high correlation coefficients *R-square*, *adjusted R-square* and *predicted R-square* were estimate (0.9355, 0.8774, and 0.924).

Acknowledgment

This research was supported by the Program of High-end Foreign Experts Working in the Educational and Cultural Sector (No. GDW20162100068), Group Project of Liaoning Provincial Department of Education (No. 2016J003), and Opening fund of Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education (No. 2017029).

References

[1] Zheng, E., *et al.*, Biological Scouring of Flax Rove with Alkalophilic Strains, *Journal of Natural Fibers*, *11* (2014), 3, pp. 256-267

[2] Jadwiga, S., *et al.*, Bio-scoUring of Linen Fabrics with Laccase Complex from Cerrena Unicolor, *Textile Research Institute*, *15* (2007), 4, pp. 63-69

[3] Magdy, K., *et al.*, A Greener Approach for Full Flax Bleaching, *The Journal of the Textile Institute*, *101* (2010), 7, pp. 674-678

[4] Zheng, H., *et al.*, An Industrial Scale Multiple Supercritical Carbon Dioxide Apparatus and Its Eco-friendly Dyeing Production, *Journal of CO_2 Utilization*, *16* (2016), Dec., pp. 272-281

[5] Zheng, H., *et al.*, An Ecofriendly Dyeing of Wool with Supercritical Carbon Dioxide Fluid, *Journal of Cleaner Production*, *143* (2017), Feb., pp. 269-277

[6] Zheng, H., *et al.*, CO_2 Utilization for the Dyeing of Yak Hair: Fracture Behavior in Supercritical State, *Journal of CO_2 Utilization*, *18* (2017), Mar., pp. 117-124

[7] Zhang, J., *et al.*, Green Dyeing of Cotton Fabrics by Supercritical Carbon Dioxide, *Thermal Science*, *19* (2015), 4, pp. 1283-1286
[8] Chen, C., *et al.*, Optimization of Dynamic Microwave-Assisted Extraction of Armillaria Polysaccharides Using RSM, and their Biological Activity, *LWT-Food Science and Technology*, *64* (2015), 2, pp. 1263-1269
[9] Barbosa, H., *et al.*, Optimization of the Supercritical Fluid Coextraction of Oil and Diterpenes from Spent Coffee Grounds Using Experimental Design and Response Surface Methodology, *The Journal of Supercritical Fluids*, *85* (2014), Jan., pp. 165-172
[10] Ara, K., *et al.*, Application of Response Surface Methodology for the Optimization of Supercritical Carbon Dioxide Extraction and Ultrasound-Assisted Extraction of Capparis Spinosa Seed Oil, *The Journal of Supercritical Fluids*, *85* (2014), Jan., pp. 173-182
[11] Gholamhossein, S., *et al.*, Application of Supercritical Carbon Dioxide to Extract Essential Oil from Cleome Coluteoides Boiss: Experimental, Response Surface Andgrey Wolf Optimization Methodology Gholamhossein, *The Journal of Supercritical Fluids*, *114* (2016), Aug., pp. 55-63
[12] Luu, T., *et al.*, Response Surface Method Applied to Supercritical Carbon Dioxide Extraction of Vetiveria Zizanioides Essential Oil, *Chemical Engineering Journal*, *155* (2009), 3, pp. 617-626

Paper submitted: February 20, 2017
Paper revised: March 6, 2017
Paper accepted: September 25, 2017